

English Translation
PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-096223

(43)Date of publication of application : 03.04.2003

(51)Int.Cl.

C08J 9/04
C08J 9/32
C08K 3/00
C08K 5/00
C08K 5/14
C08K 5/5415
C08L 83/04
//(C08L 83/04
C08L101:00)

(21)Application number : 2001-288458

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(22)Date of filing : 21.09.2001

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**(54) SILICONE RUBBER SPONGE-FORMING COMPOSITION, SILICONE RUBBER SPONGE AND
PROCESS FOR PRODUCING SAME**

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a silicone rubber sponge-forming composition that may lead to a conductive silicone rubber sponge having an even and fine foam cell, a silicone rubber sponge having an even and fine foam cell, and a production method for the same.

SOLUTION: The silicone rubber sponge-forming composition comprises (A) a polyorganosiloxane raw rubber of 100 pts.wt., (B) an inorganic filler of 1 to 500 pts.wt., (C) a thermoplastic resin hollow powder of 0.01 to 10 pts.wt., (D) a liquid compound with a boiling point being higher than room temperature of 0.1 to 10 pts.wt., (E) a heat-decomposable foaming agent of 0.1 to 10 pts.wt. and (F) a curing agent (enough quantity to cure the composition). The silicone rubber sponge is obtained by curing the composition. The production method for the same is provided.

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CLAIMS

[Claim(s)]

[Claim 1](A) Polyorganosiloxane crude rubber 100 weight section, (B) inorganic filler 1 – 500 weight section, (C) 0.01 to thermoplastics hollow granular material 10 weight section, liquefied compound 0.1 – 10 weight section in which (D) boiling point is higher than a room temperature, (E) heat decomposition type blowing agent 0.1 – 10 weight section, and the (F) hardening agent (sufficient quantity to stiffen this constituent)

A silicone rubber sponge plasticity constituent characterized by a thing, ** and others.

[Claim 2](C) The silicone rubber sponge plasticity constituent according to claim 1 in which softening temperature has a coat which consists of thermoplastics which is 40 ** – 200 **, and an ingredient contains a gas inside.

[Claim 3](C) The silicone rubber sponge plasticity constituent according to claim 2 whose thermoplastics which constitutes a coat of an ingredient is silicone resin, an acrylic resin, or polycarbonate resin.

[Claim 4](D) A silicone rubber sponge plasticity constituent of Claims 1–3 whose ingredient is water given in any 1 clause.

[Claim 5](E) A silicone rubber sponge plasticity constituent of Claims 1–4 whose ingredient is an inorganic foaming agent given in any 1 clause.

[Claim 6](E) A silicone rubber sponge plasticity constituent of Claims 1–4 whose ingredient is an organic blowing agent given in any 1 clause.

[Claim 7](A) An ingredient is polyorganosiloxane crude rubber which has at least two silicon atom joint alkenyl groups, (F) An ingredient receives platinum system catalyst [(A) ingredient 1 million weight section. For this platinum system catalyst. Platinum metal contained Range [of 0.01 to 100 weight section]]. And in one molecule at least two silicon atom absorbed water matter atoms. polyorganosiloxane which it has — [(A) A silicone rubber sponge plasticity constituent of Claims 1–6 which consist of quantity from which a ratio with the number of mols of a silicon atom absorbed water matter atom in this polyorganosiloxane to the number of mols of a silicon atom joint alkenyl group in an ingredient is set to 0.5–20] given in any 1 clause.

[Claim 8]A silicone rubber sponge plasticity constituent of Claims 1–7 which are the objects for extrusion molding given in any 1 clause.

[Claim 9]A silicone rubber sponge plasticity constituent of Claims 1–7 which are the objects for pressing using a metallic mold given in any 1 clause.

[Claim 10](A) Mix polyorganosiloxane crude rubber and the (B) inorganic filler, and a silicone rubber base is manufactured, A manufacturing method of the silicone rubber sponge plasticity constituent according to claim 1 characterized by blending the (F) hardening agent after (C) thermoplastics hollow granular material and (D) boiling point blend a liquefied compound higher than a room temperature and the (E) heat decomposition type blowing agent with this silicone rubber base after an appropriate time.

[Claim 11] Silicone rubber sponge which carries out heat cure of the silicone rubber sponge

plasticity constituent of Claims 1-9 given in any 1 clause.

[Claim 12]The silicone rubber sponge according to claim 11 whose silicone rubber sponge is a sheet shaped.

[Claim 13]The silicone rubber sponge according to claim 11 whose silicone rubber sponge has tube shape or the shape of a string.

[Claim 14]The silicone rubber sponge according to claim 11 whose silicone rubber sponge is covering material of a roll.

[Claim 15]The silicone rubber sponge according to claim 11 whose silicone rubber sponge is a gasket.

[Claim 16]A manufacturing method of silicone rubber sponge making temperature more than softening temperature of thermoplastics which constitutes the (C) ingredient heat and harden a silicone rubber sponge plasticity constituent of Claims 1-9 given in any 1 clause.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a silicone rubber sponge plasticity constituent, silicone rubber sponge, and those manufacturing methods. It is related with the silicone rubber sponge plasticity constituent which can serve as silicone rubber sponge which has a uniform and detailed foaming cell in detail, the silicone rubber sponge which has a uniform and detailed foaming cell, and those manufacturing methods.

[0002]

[Description of the Prior Art]Conventionally, the silicone rubber sponge to which silicone rubber was made to add and carry out foam curing of the foaming agent is known. This silicone rubber sponge is excellent in heat resistance and weatherability, and since it is lightweight, it is used for the use broad as the parts for cars, parts for OA equipment, etc., and the concrete target as various sealants, packing, a gasket, an O ring, roll covering material, etc. taking advantage of that characteristic.

[0003]As this silicone rubber sponge composition, For example, the silicone rubber sponge composition (refer to JP,H8-12888,A) which blended the thermal expansion nature microcapsule which expands at the temperature of 80-200 **, The silicone rubber sponge composition (refer to JP,2000-186210,A and JP,2000-309710,A) etc. which blended hollow powder with a mean particle diameter of 200 micrometers or less are proposed. However, in the silicone rubber sponge composition containing these hollow fillers, In order to obtain the sponge to which it fully foamed, it is necessary to blend a hollow filler in large quantities by a volume ratio to organopolysiloxane. There was a problem that cost cost dearly, combination of a hollow filler was difficult, or the characteristics, such as the heat resistance of silicone rubber sponge, were spoiled under the influence of the wallplate of the hollow filler to blend.

[0004]As a method of forming silicone sponge, using harmless and inexpensive water as a foaming agent, The compound which can harden an aqueous emulsion to the silicone sponge contained as a foaming agent (refer to JP,H6-20738,A), The buffer vibroisolating material made from silicone (refer to JP,H4-13738,A) etc. which contain hydrolytic drugs, such as sodium bicarbonate, as a foaming agent under water existence are proposed. However, the foaming cell of the silicone rubber sponge obtained by this method was not enough in uniformity or a detail, and it was difficult for it to satisfy the performance demanded as roll covering material.

[0005]

[Problem to be solved by the invention]This invention persons came to complete this invention, as a result of inquiring wholeheartedly that the above-mentioned problem should be canceled. That is, the purpose of this invention is to provide the silicone rubber sponge plasticity constituent which can serve as silicone rubber sponge which has a uniform and detailed foaming cell, the silicone rubber sponge which has a uniform and detailed foaming cell, and those manufacturing methods.

[0006]

[Means for Solving the Problem] "This invention, (A) polyorganosiloxane crude rubber 100 weight section, (B) The liquefied compound 0.1 – ten weight sections in which inorganic filler 1 – 500 weight section, (C) thermoplastics hollow granular material 0.01 – 10 weight section, and (D) boiling point are higher than a room temperature, (E) heat decomposition type blowing agent 0.1 – 10 weight section, and (F) hardening agent (sufficient quantity to stiffen this constituent)

A silicone rubber sponge plasticity constituent characterized by a thing, ** and others," "Silicone rubber sponge which carries out heat cure of this silicone rubber sponge plasticity constituent", "Mix (A) polyorganosiloxane crude rubber and the (B) inorganic filler, and a silicone rubber base is manufactured, To this silicone rubber base, after an appropriate time (C) thermoplastics hollow granular material, (D) After the boiling point blends a liquefied compound higher than a room temperature and the (E) heat decomposition type blowing agent, (F) A manufacturing method of said silicone rubber sponge plasticity constituent blending a hardening agent", And it is related with "a manufacturing method of silicone rubber sponge making temperature more than softening temperature of thermoplastics of the (C) ingredient heat and harden this silicone rubber sponge plasticity constituent."

[0007]

[Mode for carrying out the invention] Silicone rubber sponge which carries out heat cure of a silicone rubber sponge plasticity constituent of this invention and this silicone rubber sponge plasticity constituent to below, and those manufacturing methods are explained in detail.

(A) Polyorganosiloxane crude rubber may be the main ingredients of this invention constituent, and although it is preferred that it is straight chain shape as for the molecular structure, it may be straight chain shape with branching in part. Ranges of a weight average degree of polymerization for Motoshige are usually 1,000–20,000. (A) As a basis combined with a silicon atom in an ingredient, Alkyl groups, such as a methyl group, an ethyl group, a propyl group, a butyl group, and an octyl group; A phenyl group, Aryl groups, such as a tolyl group; substitution or unsubstituted monovalent hydrocarbon groups, such as alkyl halide groups, such as alkenyl-group; chloromethyl groups, such as a vinyl group, an allyl group, a butenyl group, a hexenyl group, and a heptenyl group, and a 3,3,3-trifluoropropyl group, are illustrated. It may have a hydroxyl group in molecular chain terminals etc. a desirable alkenyl group -- a vinyl group -- although it is subsequently a hexenyl group, a connecting position of this alkenyl group may not be limited, but may be molecular chain terminals, a chain side chain, or its both. As for the (A) ingredient, when using together a platinum system catalyst and polyorganosiloxane which has at least two silicon atom absorbed water matter atoms in one molecule as a (F) ingredient which carries out a postscript, it is preferred to have at least two alkenyl groups in one molecule. As for a basis combined with silicon atoms other than an alkenyl group, it is preferred that it is a methyl group.

[0008] As a desirable (A) ingredient, chain both-ends dimethylvinyl siloxy group blockade polydimethyl siloxane crude rubber, Chain both-ends trimethylsiloxy group blockade polydimethyl siloxane crude rubber, Chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber, Chain both-ends dimethylvinyl siloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber, Chain both-ends dimethylhydroxy siloxy group blockade polydimethyl siloxane crude rubber, Chain both-ends dimethylhydroxy siloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber, Chain both-ends methylvinyl hydroxy siloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber, Chain both-ends dimethylhexenyl siloxy group blockade polydimethyl siloxane crude rubber, Chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylhexenyl siloxane copolymer crude rubber, chain both-ends dimethylhexenyl siloxy group blockade dimethylsiloxane methylhexenyl siloxane copolymer crude rubber, Chain both-ends dimethylvinyl siloxy group blockade dimethylsiloxane methylphenyl siloxane copolymer crude rubber, Chain both-ends dimethylhexenyl siloxy group blockade dimethylsiloxane methylphenyl siloxane copolymer crude

rubber, Chain both-ends dimethylvinyl siloxy group blockade dimethylsiloxane methyl (3,3,3-trifluoropropyl) siloxane copolymer crude rubber, Two or more sorts of mixtures, chain both-ends dimethylhexenyl siloxy group blockade dimethylsiloxane methyl (3,3,3-trifluoropropyl) siloxane copolymer crude rubber and these polyorganosiloxane crude rubber, are illustrated.

[0009](B) As an inorganic filler, impalpable powder-like silica, such as dry process silica and wet process silica, Those surfaces Organochlorosilane, organoalkoxysilane, The reinforcement nature bulking agent illustrated by the impalpable powder-like silica etc. by which hydrophobing processing was carried out by hexa ORGANO disilazane, an organosiloxane oligomer, etc.; The end of quartz powder, A semi- reinforcement nature bulking agent thru/or increase-in-quantity bulking agents, such as diatomite, heavy calcium carbonate, precipitated calcium carbonate, magnesium oxide, silicic-acid calcium, mica, an aluminum oxide, and aluminium hydroxide, are illustrated. Since combination for the (A) ingredient will become difficult if too large, the loadings for Motoshige are 1 - 500 weight section to (A) ingredient 100 weight section, a reinforcement nature bulking agent has 1 - 100 preferred weight section, and a semi- reinforcement nature bulking agent thru/or an increase-in-quantity nature bulking agent have 1 - 300 preferred weight section.

[0010]It does not interfere, unless the purpose of this invention is spoiled, even if it chooses a conductive bulking agent as a (B) ingredient, in order to give conductivity to a silicone rubber sponge composition. As this conductive bulking agent, carbon system conducting agent; gold, such as carbon black, carbon fiber, and graphite, Metal-powder; conductive zinc oxides, such as silver and nickel, conductive titanium oxide, a conductive aluminum oxide; the conductive bulking agent which carried out electric conduction coating treatment to the various filler surfaces on the filler surface, such as carrying out metal plating processing, is illustrated. Even if it uses these conductivity bulking agent together with an inorganic filler and uses it alone, it does not interfere, and even if it uses together two or more kinds of conductive fillers, unless the purpose of this invention is spoiled, it does not interfere. As for especially the (B) ingredient, since good conductivity is obtained by a little addition, it is preferred that it is carbon black. Although what is usually regularly used by the conductive rubber constituent can be used as desirable carbon black, in order to avoid hardening inhibition of this invention constituent, it is preferred that it is carbon black of pH six to 10 range manufactured from the low-sulfur raw material. As for the loadings of these conductive bulking agents, it is preferred to be 1 - 200 weight section and to consider it as 5-100 copies especially to (A) ingredient 100 weight section. This is because sponge may be hard to be obtained if conductivity is obtained as it is less than the minimum of a mentioned range, it may not be and the maximum of a mentioned range is surpassed.

[0011]While (C) thermoplastics hollow powder used for this invention becomes a core of the foaming cell formed into the silicone rubber sponge produced by making carry out heat cure of this invention constituent, it serves to make the size of the foaming cell uniform. This (C) ingredient is hollow powder which contains a gas in the inside by using thermoplastics as a coat. Here, as desirable thermoplastics, silicone resin, an acrylic resin, and polycarbonate resin are illustrated. As for the softening temperature of this thermoplastics, 40-200 °C is preferred, and its 60-180 °C is more preferred. As a gas included by this hollow granular material, inactive gas, such as air or nitrogen gas, and gaseous helium, is preferred. (C) The size of an ingredient has a preferred range in which the mean particle diameter is 0.1-500 micrometers, and its range which is 1-50 micrometers is more preferred. This (C) ingredient sprays the dispersion liquid of the thermoplastics and water which dissolved in the solvent in a heat style from a spray nozzle, for example, and it is manufactured by carrying out disintegration of the thermoplastics while dispersing an organic solvent. The loadings for Motoshige are 0.01 - 10 weight section to (A) ingredient 100 weight section, and it is preferred that it is 0.1 - 5 weight section.

[0012](D) When the liquid which has the boiling point higher than a room temperature carries out heat cure of this invention constituent and forms silicone rubber sponge, in order to volatilize, to carry out the work as a foaming agent and to form a uniform and detailed foaming cell with the (C)

ingredient and the (E) ingredient mentioned later, it is an ingredient made indispensable. This is because this liquid volatilizes and good silicone rubber sponge may not no longer be obtained, while keeping this invention constituent if the boiling point is lower than a room temperature.

Corresponding to the formation method and its formation condition of silicone rubber sponge as a (D) ingredient, Although what is necessary is just to select what has the suitable boiling point higher than a room temperature, it is preferred that it is a liquid which generally has the boiling point of the range of 25–200 **, and it is more preferred that it is a liquid which has the boiling point of the range which is 50–180 **.

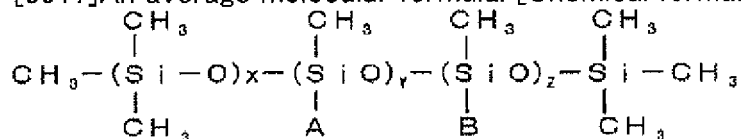
[0013]It is necessary to dissolve a wallplate of the (C) ingredient during storage of this invention constituent or, when carrying out heat cure of this invention constituent and forming conductive silicone rubber sponge, heating does not need to decompose, or the (D) ingredient does not need to be accompanied by a chemical reaction with other ingredients.

[0014]As this (D) ingredient, water; methanol, ethanol, 1-propanol, Alcohols, such as cyclohexanol; Ethylene glycol monoethyl ether, Ethylene glycol derivatives, such as ethylene glycol monoethyl ether acetate; Hexamethyl cyclotrisiloxane, annular dimethylsiloxane oligomer [such as octamethylcyclotetrasiloxane,]; -- chain both-ends trimethylsiloxy group blockade dimethylsiloxane oligomer; -- chain both-ends dimethylhydroxy siloxy group blockade dimethylsiloxane oligomer. And two or more sorts of these mixtures are illustrated. Water is the most preferred in these and, subsequently annular dimethylsiloxane oligomer is preferred. Water with purity high as water called pure water, purified water, ion exchange water, etc. is preferred.

[0015](D) Although an ingredient may be directly blended with a silicone rubber base which mixes the (A) ingredient and the (B) ingredient, it aims at improvement in the handling nature of the (D) ingredient, or improvement in dispersibility to a silicone rubber base, (D) Even if it blends an ingredient with a silicone rubber base with a form of a mixture with adsorption granular materials, such as thickening agents, such as silica powder, and porous powder, unless the purpose of this invention is spoiled, don't interfere. When the (D) ingredient is water, blending a mixture and silicone oil with water-soluble silicone in a form of an emulsion of a water-in-oil type made into an oil reservoir does not interfere, either, unless the purpose of this invention is spoiled.

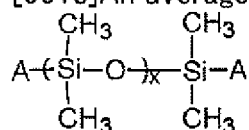
[0016](D) When choosing water as an ingredient and blending with a silicone rubber base as a mixture with water-soluble silicone, the water-soluble silicone should just be silicone which can be dissolved in water, and the kind in particular is not limited. Although loadings in particular to water of water-soluble silicone are not limited, it is preferred that it is 1 to 80 weight %, and it is especially preferred that it is 5 to 70 weight %. As silicone which can be dissolved in this water, although polyoxyalkylene modified silicone oil, amino alkyl-group content silicone oil, amide group content silicone oil, a carbinol group content siloxane oligomer, etc. are mentioned, Polyoxyalkylene modified silicone oil is preferred also in these. Organopolysiloxane which has a polyoxyalkylene group as this polyoxyalkylene modified silicone oil at a side chain or an end as shown with the following average molecular formula is illustrated.

[0017]An average molecular formula: [Chemical formula 1]



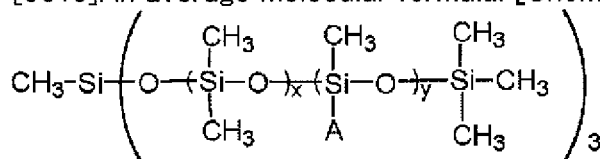
{x and y are one or more integers among a formula, and z is 0 or one or more integers. A is general formula: $-(\text{CH}_2)_a - \text{O} - (\text{C}_2\text{H}_4\text{O})_p - (\text{C}_3\text{H}_6\text{O})_q - \text{R}$ (among a formula). As for an integer of 1–3, and p, one or more integers and q of a are 0 or one or more integers, R is an alkyl group with 1–4 carbon atoms, such as a hydrogen atom or a methyl group, an ethyl group, and a propyl group. It is an organic group shown and B is an organic group shown by general formula: $-(\text{CH}_2)_n - \text{CH}_3$ (n is an integer of 7–23 among a formula.). }

[0018]An average molecular formula: [Chemical formula 2]



(x and A are the same as the above among a formula.)

[0019]An average molecular formula: [Chemical formula 3]

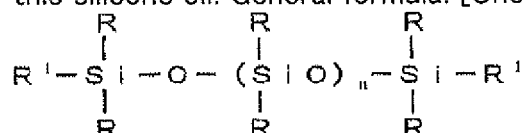


(x, y, and A are the same as the above among a formula.)

[0020]In order for this polyoxyalkylene modified silicone oil to acquire good water solubility, a polyoxyalkylene portion is a polyoxyethylene or an oxyethylene oxypropylene copolymer, and that in which the content in a molecule is 50 weight % or more is preferred.

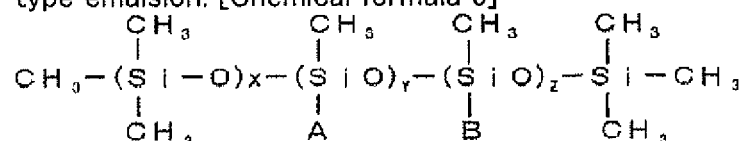
[0021] Water is chosen as a (D) ingredient, and when blending with a silicone rubber base as a water-in-oil type emulsion which made silicone oil an oil reservoir, this water-in-oil type emulsion is easily manufactured by distributing water in silicone oil with a surface-active agent. Although content in particular of water in this water-in-oil type emulsion is not limited, it is preferred that it is 1 to 80 weight %, and it is especially preferred that it is 20 to 70 weight %.

[0022]The silicone oil used as an oil reservoir is oligomer thru/or polymer which makes JIORUGANO siloxane units a main skeleton, the shape of liquid is presented and the kind in particular should not just be limited. The following diorganopolysiloxane is illustrated as an example of representation of this silicone oil. General formula: [Chemical formula 4]



(R is a monovalent hydrocarbon group or an alkyl halide group among a formula, and R¹ is R or a hydroxyl group.) As a monovalent hydrocarbon group, a methyl group, an ethyl group, a propyl group, a butyl group, Aralkyl groups, such as cycloalkyl group; beta-phenylethyl groups, such as alkenyl-group; cyclohexyl groups, such as alkyl-group; vinyl groups, such as a pentyl group and a hexyl group, an allyl group, and a hexenyl group; Aryl groups, such as a phenyl group, etc. are illustrated. As an alkyl halide group, 3-chloropropyl group and a 3,3,3-trichloropropyl group are illustrated. An alkyl group, especially a methyl group are preferred also in these. n is zero or more integers. It is expressed, and the viscosity at 25 °C is within the limits of 1 - 100,000 mPa·s, and is within the limits of 10 - 100,000 mPa·s preferably.

[0023]As a surface-active agent, what is necessary is just a surface-active agent which can form a water-in-oil type emulsion, and if hardening inhibition is not caused, the kind in particular will not be limited. Diorganopolysiloxane, a general formula which have a polyoxyalkylene group in a side chain as shown with a following general formula as a surface-active agent for forming this water-in-oil-type emulsion: [Chemical formula 5]



(x, y, z, A, and B are as aforementioned among a formula.) -- a polydimethyl siloxane which has a

polyoxyalkylene group shown by the above-mentioned formula A in molecular chain terminals. Polyoxyethylene sorbitan fatty acid ester, polyoxyethylene sorbitol fatty acid ester, A mixture of non-ion system surface-active agents, such as polyethylene glycol fatty acid ester, polyoxyethylene alkyl ether, and polyoxyethylene alkyl phenyl ether, and the above-mentioned polyoxyalkylene group content organopolysiloxane and the above-mentioned non-ion system surface-active agent is illustrated. (D) Loadings of an ingredient are 0.01 – 10 weight section to (A) ingredient 100 weight section. This is because it stops fully working as a foaming agent when a cell of silicone sponge which will be fabricated if a maximum of a mentioned range is exceeded becomes uneven easily and less than a minimum of a mentioned range becomes.

[0024](E) When a heat decomposition type blowing agent carries out heat cure of this invention constituent and forms silicone rubber sponge, in order to serve to assist the (D) ingredient and to form a uniform and detailed foaming cell with the (C) ingredient and the (D) ingredient, it is an ingredient made indispensable. As this heat decomposition type blowing agent, the conventionally publicly known inorganic foaming agent and/or organic blowing agent which are used for the silicone rubber sponge composition can be used.

[0025]As an inorganic foaming agent, sodium bicarbonate, potassium bicarbonate, sodium borohydride, calcium azido, etc. are illustrated. Sodium bicarbonate is especially preferred.

[0026]As an organic blowing agent, azobisisobutyronitrile, 2, and 2'-azobis (2,4-dimethylvaleronitrile), Azo compound;N,N'-dinitrosopentamethylenetetramines, such as dimethyl- 2,2'-azobisisobutyrate and an azodicarbonamide, Nitroso compounds, such as N,N'-dimethyl- N,N'-dinitroso terephthalamide; p-tosyl hydrazide, Sulfonylhydrazide compound;2-propenoic acid hydrazide, such as 4,4'-oxybis benzene sulfonylhydrazide and diphenylsulfone-3,3'-disulfonylhydrazide, Carbonyl hydrazine compounds, such as acetylhydrazine; diazido compounds, such as 4,4'-diazide diphenyl, 4,4'-diazido benzophenone, and 2,5-diazido toluene, etc. are illustrated. The amount of Motoshige may use together and use one kind of heat decomposition type blowing agents [two or more kinds of].

[0027](E) The loadings of an ingredient are 0.1 – 10 weight section to (A) ingredient 100 weight section, and it is preferred that it is 0.1 – 1.0 weight section. This is because hardening inhibition may be caused or the heat resistance of the silicone rubber sponge obtained may get worse, when the silicone rubber sponge to which it fully foamed is not obtained in case of less than the minimum of a mentioned range but the maximum of a mentioned range is exceeded.

[0028](F) A hardening agent is an ingredient for stiffening this invention constituent, and the kind in particular is not limited. Organic peroxide is mentioned as a typical hardening agent. As such organic peroxide, benzoyl peroxide, di-t-butyl peroxide, 2,5-dimethyl- 2,5-di(tert-butylperoxy) hexane, Bis (ortho-methylbenzoyl) peroxide, bis(meta-methylbenzoyl) peroxide, Dimethylbenzoyl peroxide, such as monomethylbenzoyl peroxide, such as bis(****- methylbenzoyl)peroxide, and bis(2,4-dimethylbenzoyl)peroxide, bis(2,4,6-trimethyl benzoyl)peroxide **, etc. are illustrated. The loadings for Motoshige are 0.1 – 10 weight section to mixture 100 weight section of a (A) ingredient – (D) ingredient.

[0029]In being what has the alkenyl group that (A) polyorganosiloxane crude rubber is represented with a vinyl group, in [at least two] one molecule, Hardening by an addition hardening reaction is possible for this invention constituent, and into one molecule, it can use together the polyorganosiloxane and the platinum system catalyst containing at least two silicon atom absorbed water matter atoms, and can use them as a hardening agent. Since the concomitant use of this polyorganosiloxane and a platinum system catalyst can change hardenability arbitrarily, it is preferred as a hardening agent of this invention constituent.

[0030]As such polyorganosiloxane, A chain both-ends trimethylsiloxy group blockade polymethyl hydrogen siloxane, A chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane copolymer, A chain both-ends dimethyl hydrogen siloxy group blockade dimethylsiloxane methylhydrogensiloxane copolymer, An annular dimethylsiloxane

methylhydrogensiloxane copolymer, The siloxane units expressed per annular polymethyl hydrogen siloxane and formula: $(\text{CH}_3)_3\text{SiO}_{1/2}$, Formula : $(\text{CH}_3)_2\text{HSiO}_{1/2}$ The organopolysiloxane which consists of siloxane units shown by siloxane-units [which are expressed per $2\text{HSiO}_{1/2}$], and formula: $\text{SiO}_{4/2}$, Formula : $(\text{CH}_3)_2\text{HSiO}_{1/2}$ The siloxane units expressed per organopolysiloxane [which consists of siloxane units shown per siloxane-units / which are expressed per $2\text{HSiO}_{1/2}$ /, and formula: $\text{CH}_3\text{SiO}_{3/2}$], and formula: $(\text{CH}_3)_2\text{HSiO}_{1/2}$, The formula : $(\text{CH}_3)_2\text{SiO}_{2/2}$ unit, and a formula : The organopolysiloxane which consists of siloxane units shown per $\text{CH}_3\text{SiO}_{3/2}$, A chain both-ends dimethyl hydrogen siloxy group blockade polydimethyl siloxane, A chain both-ends dimethyl hydrogen siloxy group blockade dimethylsiloxane methylphenyl siloxane copolymer, Two or more sorts of mixtures, chain both-ends dimethyl hydrogen siloxy group blockade dimethylsiloxane methyl (3,3,3-trifluoropropyl) siloxanes and such polyorganosiloxanes, are illustrated. Although the viscosity in particular at 25 °C of this polyorganosiloxane is not limited, it is preferred that it is the range of 2 – 100000 mPa·s. The addition needs to be quantity that the ratio of the number of sum total mols of the silicon atom absorbed water matter atom in this polyorganosiloxane and the number of sum total mols of the alkenyl group in the (A) ingredient becomes – (0.5:1) (20:1).

[0031]As a platinum system catalyst, in this case, the denaturing alcohol thing of particle platinum, chloroplatinic acid, and chloroplatinic acid, Chelate compound of platinum, platinum and the complex of diketone, chloroplatinic acid and the coordinated complex of olefins, The complex of chloroplatinic acid and an alkenyl siloxane, and these Alumina, The thing which carriers, such as silica and carbon black, were made to support is illustrated, and also in these, since activity is high as a catalyst for a hydrosilylation reaction, the complex of chloroplatinic acid and an alkenyl siloxane is preferred, A platinum alkenyl siloxane complex which is indicated by especially JP,S42-22924,B is preferred. The spherical-particles catalyst which comprises thermoplastics which uses a platinum system catalyst as a platinum metal atom, and contains it 0.01weight % or more can also be used. As for the quantity of the platinum metal in a platinum system catalyst, it is preferred that it is within the limits of 0.01 – 500 weight section to (A) ingredient 1 million weight section, and it is especially preferred that this is within the limits of 0.1 – 100 weight section.

[0032]In using together a platinum system catalyst and the polyorganosiloxane which has at least two silicon atom absorbed water matter atoms in one molecule as a (F) ingredient, In order to raise the handling workability and storage stability of this invention constituent, a 2-methyl-3-butyn-2-ol, A 2-phenyl-3-butyn-2-ol, 3,5-dimethyl-1-hexyn-3-ol, Acetylene series compound; 3,5-dimethyl-1-hexene-1-yne, such as 1-ethynyl-1-cyclohexanol, 1,5-hexadiyne, and 1,6-heptadiyne, Ene-yne compound; 1,3-divinyl tetramethyl disiloxane, such as 3-ethyl-3-butene-1-yne and 3-phenyl-3-butene-1-yne, 1, 3, 5, 7-tetravinyl tetramethyl cyclotetrasiloxane, alkenyl siloxane oligomer [, such as a 1,3-divinyl- 1,3-diphenyl dimethyldi siloxane,]; -- ethynyl group content silicon compound [, such as methyltris (3-methyl-1-butyne-3-oxo) Silang,]; -- tributylamine. Phosphorus content compounds, such as nitrogen containing compound; triphenyl phosphine, such as tetramethylethylenediamine and benzotriazole; In addition to this, a sulfur content compound, It is preferred to blend hardening depressants, such as a hydro-peroxy compound, maleic acid derivatives, and two or more sorts of these mixtures.

[0033]Three or less weight sections may be sufficient as the loadings of these hardening depressants to (A) ingredient 100 weight section, they are usually 0.001 – 3 weight section, and are 0.01 – 1 weight section preferably. A desirable hardening depressant is the acetylene series compound which was illustrated above, and these demonstrate sufficient preservation stability of a constituent, and quick hardenability with sufficient balance.

[0034]As arbitrary ingredients, in addition, pyrogenic silica, aluminium hydroxide, an aluminum oxide, The end of quartz powder, diatomite, an aluminosilicate, heavy calcium carbonate, precipitated calcium carbonate, Heat-resistant agents, such as paints; cerium oxide, such as inorganic filler; iron

oxide, such as magnesium oxide, silicic-acid calcium, and mica, and a titanium dioxide, and hydroxylation cerium; fire retardant, such as manganese carbonate, zinc carbonate, and fumed titanium dioxide, may be contained. These inorganic fillers may use what could use the unsettled thing and was beforehand processed by the finishing agent.

[0035] Furthermore to this invention constituent, a chain both-ends trimethylsiloxy group blockade polydimethyl siloxane, A chain both-ends dimethylhydroxy siloxy group blockade polydimethyl siloxane, A chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylphenyl siloxane copolymer, A chain both-ends trimethylsiloxy group blockade dimethylsiloxane diphenyl siloxane copolymer, A chain both-ends dimethylhydroxy siloxy group blockade dimethylsiloxane methylphenyl siloxane copolymer, A chain both-ends trimethylsiloxy group blockade dimethylsiloxane methyl (3,3,3-trifluoropropyl) siloxane copolymer etc., Liquefied polyorganosiloxane which does not have a silicon atom joint alkenyl group and a silicon atom absorbed water matter atom; Silicone rubber powder, Silicone powdered additive agents, such as silicone resin powder; mold lubricant; adhesion promoters, such as stearic acid, calcium stearate, zinc stearate, and cerium stearate, etc. may be contained.

[0036] Although this invention constituent can be easily manufactured the above (A) ingredient - (F) ingredients or by adding other ingredients if needed further and mixing uniformly, (B) When it contains a reinforcement nature bulking agent as an ingredient, after mulling the finishing agent of a reinforcement nature bulking agent under heating the (A) ingredient, this reinforcement nature bulking agent, and if needed and manufacturing a silicone rubber base, mixing with other ingredients is preferred. As a manufacturing installation, mixed equipment or kneading apparatus, such as a kneader mixer and a continuation extruding kneading machine, are illustrated.

[0037] What is necessary is to heat this invention constituent to the temperature more than the softening temperature of the thermoplastics which constitutes the (C) ingredient, and just to stiffen it, in order to manufacture silicone rubber sponge from this invention constituent. In that case, it is hardened foaming to this invention constituent, and forms silicone rubber sponge. Since this invention constituent can form good silicone rubber sponge also in extrusion molding and the pressing which used the metallic mold, The silicone rubber sponge of various form, such as a sheet shaped, ring shape, the shape of string, and tube shape, can be fabricated, and there is the feature of being suitable also for production of a composite molding thing with metal or other organic resin. The silicone rubber sponge obtained in this way has a uniform and detailed foaming cell, for example, is useful as the gasket for airtight maintenance of a structural component, a fire-resistant gasket, a sealant, an O ring, a cushioning material, a surface coating material of a copying machine roll, etc.

[0038]

[Working example] Next, an working example and a reference example explain this invention. There is a weight section among an working example with a part, and viscosity is a value at 25 **.

[0039]

[Reference example 1] It comprises methyl siloxane units and methylphenyl siloxane units, The mole ratio made the solution (30 weight % of the amounts of solid content) which dissolved in dichloromethane silicone resin (80 ** of softening temperatures, specific gravity 1.20) which is 22:78 100-cc the amount of supply for /, carried out liquid transport of the pure water into the dynamic mixer by 25-cc the amount of supply for /, was mixed, and considered it as the water dispersion. Subsequently, it sprayed continuously in the spray dryer which made this water dispersion the nitrogen gas air current using 2 hydraulic nozzles. The heat style temperature of the nitrogen gas at this time was 70 **, and the pressures were 0.05MPa. The obtained silicone resin hollow granular material was immersed in the solution which consists of 100 copies of pure water, and one copy of nonionic surface active agent (ethyleneoxide addition of trimethyl nonanol) for 24 hours, and the silicone resin hollow granular material which floated was classified and caught. Mean particle diameter is 40 micrometers, the average thickness of the coat is 4 micrometers, and the obtained silicone resin hollow granular material had included nitrogen gas to the inside.

[0040]

[Reference example 2] an average molecular formula $--\text{Me}_3\text{SiO}-(\text{Me}_2\text{SiO})_7--\text{Me}$ is a methyl group among a $7-(\text{MeR}^2\text{SiO})_3-\text{SiMe}_3$ type, and R^2 shows the basis expressed with formula: $-(\text{CH}_2)_2-\text{O}-(\text{C}_2\text{H}_4\text{O})_{12}-\text{H}$. 40 copies of water-soluble polyoxyalkylene modified silicone oil and 60 copies of ion exchange water of viscosity 400 mPa-s which are shown by] were uniformly mixed in the flask, and solution (the following, the solution A) was prepared.

[0041]

[Reference example 3] an average molecular formula $--\text{Me}_3\text{SiO}-(\text{Me}_2\text{SiO})_7--\text{Me}$ and R^2 are the same as that of the above among a $0-(\text{MeR}^2\text{SiO})_3-\text{SiMe}_3$ type. 50 copies of chain both-ends trimethylsiloxy group blockade polydimethyl siloxanes of ten copies of polyoxyalkylene modified silicone oil of viscosity 1600 mPa-s and viscosity 100 mPa-s shown by] were put into the flask, and were stirred strongly. Subsequently, the water-in-oil type emulsion which made the oil reservoir the chain both-ends trimethylsiloxy group blockade polydimethyl siloxane of viscosity 100 mPa-s was prepared by adding 40 copies of ion exchange water gradually to this, and mixing to it.

[0042]

[Work example 1] 100 copies of chain both-ends dimethylvinyl siloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber which consists of 99.85 mol of dimethylsiloxane unit %, and 0.15 mol of methylvinyl siloxane-units % (degree of polymerization 3000), It mulled until it put 40 copies of dry process silica of specific surface area [of 200 m] ²/g by ten copies of chain both-ends dimethylhydroxy siloxy group blockade dimethylsiloxane oligomer of viscosity 60 mPa-s, and a BET adsorption method into the kneader mixer and became bottom homogeneity of heating, and the silicone rubber base was produced. Subsequently, 100 copies of this silicone rubber base is received, 1.0 copy (this chain both-ends trimethylsiloxy group blockade dimethylsiloxane methyl hydrogen SHIROKI.) of chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane copolymer of 25 mPa-s (0.8 weight % of silicon atom absorbed water matter atom content) The quantity from which the ratio of the number of mols of the silicon atom absorbed water matter atom in the Sun copolymer and the number of mols of the silicon atom joint vinyl group in the above-mentioned vinyl group content polydyorganosiloxane crude rubber is set to 4.9, As a hydrosilylation reaction inhibitor, 0.015 copy of 1-ethynyl-1-cyclohexanol, The complex (0.6 weight % of platinum content) of chloroplatinic acid and tetramethyl divinyl disiloxane 0.06 copy, 1.0 copy of silicone resin hollow granular material, 0.5 copy of distilled water, and 0.5 copy of sodium bicarbonate which were obtained by the reference example 1 were added, it mulled uniformly on 2 rolls, and the silicone rubber sponge plasticity constituent was obtained. After making this constituent into a 5-mm-thick sheet shaped, put in a 250 ** heating furnace, and heat for 10 minutes, it was made to harden, and the silicone rubber sponge sheet was obtained. When the foaming cell of this silicone rubber sponge sheet was observed, the foaming cell was almost uniform and the size of that cell was 0.1-0.4 mm in diameter.

[0043]

[Work example 2] After feeding into 1 axis extrusion machine of 65 mmphi the silicone rubber sponge plasticity constituent obtained in working example 1 and extruding as tube shape mold goods, it heated for 4 minutes all over a 250 ** heating furnace, and the silicone rubber sponge tube was obtained. The foaming cell of this silicone rubber sponge tube was almost uniform, and the size of that foaming cell was 0.1-0.5 mm in diameter.

[0044]

[Work example 3] The form of the cavity taught 16 cm of 10 mmx constituent [which was obtained in working example 1 / silicone rubber sponge plasticity] ³ to the compression mold in which it is a rectangular parallelepiped which are 40 mm x 80 mm, and the capacity is 32cm³, it heated for 15

minutes at 170 **, and the silicone rubber sponge molded product was obtained. The outside of this silicone rubber sponge molded product was faithful to the cavity form of a metallic mold, and the size of that foaming cell was 0.1–0.4 mm in diameter, and was almost uniform.

[0045]

[Work example 4] 100 copies of chain both-ends dimethylvinyl siloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber which consists of 99.85 mol of dimethylsiloxane unit %, and 0.15 mol of methylvinyl siloxane-units % (degree of polymerization 3000), It mulled until it put 40 copies of dry process silica of ten copies of chain both-ends dimethylhydroxy siloxy group blockade dimethylsiloxane oligomer [of viscosity 60 mPa·s], and specific surface area [of 200 m]²/g into the kneader mixer and became bottom homogeneity of heating, and the silicone rubber base was produced. Subsequently, 100 copies of this silicone rubber base is received, 1.0 copy (this chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane.) of trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane copolymer of 25 mPa·s (0.8 weight % of silicon atom absorbed water matter atom content) The quantity from which the ratio of the number of mols of the silicon atom absorbed water matter atom in a copolymer and the number of mols of the silicon atom joint vinyl group in the above-mentioned vinyl group content polydyorganosiloxane crude rubber is set to 4.9, As a hydrosilylation reaction inhibitor, 0.015 copy of 1-ethynyl-1-cyclohexanol, The complex (0.6 weight % of platinum content) of chloroplatinic acid and tetramethyl divinyl disiloxane 0.06 copy, 1.0 copy of silicone resin hollow granular material, 0.5 copy of distilled water which were obtained by the reference example 1, 0.5 copy of azodicarbonamide system organic blowing agent with a decomposition temperature of 122 ** (trade name BINIHORUAK#2), 0.5 copy of 2, 5-dimethyl- 2, and 5-JI (tertiary butyl peroxy) hexane were added as a hardening auxiliary agent, it mulled uniformly on 2 rolls, and the silicone rubber sponge plasticity constituent was obtained. After making this constituent into a 5-mm-thick sheet shaped, put in a 250 ** heating furnace, and heat for 10 minutes, it was made to harden, and the silicone rubber sponge sheet was obtained. When the foaming cell of this silicone rubber sponge sheet was observed, the foaming cell was almost uniform and the size of that cell was 0.1–0.4 mm in diameter.

[0046]

[Work example 5] Form of a cavity taught 10 cm of 10 mmx constituent [which was obtained in working example 4 / silicone rubber sponge plasticity]³ to a compression mold in which it is a rectangular parallelepiped which are 40 mm x 80 mm, and the capacity is 32cm³, it heated for 15 minutes at 170 **, and a silicone rubber sponge molded product was obtained. An outside of this silicone rubber sponge molded product was faithful to cavity form of a metallic mold, and a size of that foaming cell was 0.1–0.5 mm in diameter, and was almost uniform.

[0047]

[Work example 6] 100 copies of chain both-ends dimethylvinyl siloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber which consists of 99.85 mol of dimethylsiloxane unit %, and 0.15 mol of methylvinyl siloxane-units % (degree of polymerization 3000), It mulled until it put 20 copies of dry process silica of five copies of chain both-ends dimethylhydroxy siloxy group blockade dimethylsiloxane oligomer [of viscosity 60 mPa·s], and specific surface area [of 200 m]²/g into a kneader mixer and became bottom homogeneity of heating, and a silicone rubber base was obtained. It mulled until it added 15 copies of acetylene black (DENKA black; made by DENKI KAGAKU KOGYO KABUSHIKI KAISHA) to 125 copies of this silicone rubber base and became uniform at a room temperature in it, and a conductive silicone rubber base was produced. Subsequently, 100 copies of this conductive silicone rubber base is received, 1.0 copy (this chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane.) of trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane copolymer of 25 mPa·s (0.8 weight % of silicon atom absorbed water matter atom content) Quantity from which a ratio of the number of mols of a silicon atom absorbed water matter atom in a copolymer and the number of mols of a silicon atom

joint vinyl group in the above-mentioned vinyl group content polydyorganosiloxane crude rubber is set to 4.5, As a hydrosilylation reaction inhibitor, 0.015 copy of 1-ethynyl-1-cyclohexanol, A complex (0.6 weight % of platinum content) of chloroplatinic acid and tetramethyl divinyl disiloxane 0.06 copy, 1.0 copy of silicone resin hollow granular material, 0.5 copy of distilled water, and 0.5 copy of sodium bicarbonate which were obtained by the reference example 1 were added, it mulled uniformly on 2 rolls, and a conductive silicone rubber sponge plasticity constituent was obtained. After making this constituent into a 5-mm-thick sheet shaped, put in a 250 ** heating furnace, and heat for 10 minutes, it was made to harden, and a conductive silicone rubber sponge sheet was obtained. When a foaming cell of this conductive silicone rubber sponge sheet was observed, a foaming cell was almost uniform and a size of that cell was 0.1-0.4 mm in diameter.

[0048]

[Work example 7]After feeding into 1 axis extrusion machine of 65 mmphi a conductive silicone rubber sponge plasticity constituent obtained in working example 6 and extruding as tube shape mold goods, it heated for 4 minutes all over a 250 ** heating furnace, and a conductive silicone rubber sponge tube was obtained. A foaming cell of this conductive silicone rubber sponge tube was almost uniform, and a size of that foaming cell was 0.1-0.5 mm in diameter.

[0049]

[Work example 8]It is a rectangular parallelepiped whose form of a cavity is 10mmx40mmx80mm, The capacity taught 16 cm of conductive silicone rubber sponge plasticity constituent ³ obtained in working example 6 to a compression mold which is 32cm³, it heated for 15 minutes at 170 **, and a conductive silicone rubber sponge molded product was obtained. An outside of this conductive silicone rubber sponge molded product was faithful to cavity form of a metallic mold, and a size of that foaming cell was 0.1-0.4 mm in diameter, and was almost uniform.

[0050]

[Work example 9]In an working example 6, a conductive silicone rubber sponge plasticity constituent was obtained like an working example 6 except having added 1.0 copy of solution A which was changed into distilled water and produced by the reference example 2 to 100 copies of conductive silicone rubber bases. After making this constituent into a 5-mm-thick sheet shaped, it supplies to 250 ** oven, heat cure was carried out to it for 10 minutes, and a conductive silicone rubber sponge sheet was obtained. A foaming cell of this conductive silicone rubber sponge sheet was uniform, and a size of that foaming cell was 0.1-0.5 mm in diameter.

[0051]

[Work example 10]In an working example 6, a conductive silicone rubber sponge plasticity constituent was obtained like an working example 6 except having added 1.2 copies of water-in-oil type emulsions which were changed into distilled water and produced by the reference example 3 to 100 copies of conductive silicone rubber base compounds. After making this constituent into a 5-mm-thick sheet shaped, it supplies to 250 ** oven, heat cure was carried out to it for 10 minutes, and a conductive silicone rubber sponge sheet was obtained. A foaming cell of this conductive silicone rubber sponge sheet was uniform, and a size of that foaming cell was 0.1-0.5 mm in diameter.

[0052]

[Work example 11]100 copies of chain both-ends dimethylvinyl siloxy group blockade organopolysiloxane crude rubber which consists of 99.85 mol of dimethylsiloxane unit %, and 0.15 mol of methylvinyl siloxane-units % (degree of polymerization 3000), It mulled until it put five copies of chain both-ends dimethylhydroxy siloxy group blockade dimethylsiloxane oligomer of viscosity 60 mPa-s, and 40 copies of wet process silica of specific surface area [of 200 m] ²/g into a kneader mixer and became bottom homogeneity of heating, and a silicone rubber base was produced. Subsequently, 100 copies of this silicone rubber base is received, 1.0 copy (this chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane.) of trimethylsiloxy group

blockade dimethylsiloxane methylhydrogensiloxane copolymer of 25 mPa-s (0.8 weight % of silicon atom absorbed water matter atom content) Quantity from which a ratio of the number of mols of a silicon atom absorbed water matter atom in a copolymer and the number of mols of a silicon atom joint vinyl group in the above-mentioned vinyl group content polydyorganosiloxane crude rubber is set to 4.6, As a hydrosilylation reaction inhibitor, 0.015 copy of 1-ethynyl-1-cyclohexanol, A complex (0.6 weight % of platinum content) of chloroplatinic acid and tetramethyl divinyl disiloxane 0.06 copy, 1.0 copy of silicone resin hollow granular material, 0.5 copy of distilled water, and 0.5 copy of sodium bicarbonate which were obtained by the reference example 1 were added, it mulled uniformly on 2 rolls, and a silicone rubber sponge plasticity constituent was obtained. After making this constituent into a 5-mm-thick sheet shaped, put in a 250 ** heating furnace, and heat for 10 minutes, it was made to harden, and a silicone rubber sponge sheet was obtained. When a foaming cell of this silicone rubber sponge sheet was observed, a foaming cell was almost uniform and a size of that cell was 0.1-0.4 mm in average diameter.

[0053]

[Work example 12] 100 copies of chain both-ends dimethylvinyl siloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber which consists of 99.85 mol of dimethylsiloxane unit %, and 0.15 mol of methylvinyl siloxane-units % (degree of polymerization 3000), It mulled until it put 40 copies of dry process silica of ten copies of chain both-ends dimethylhydroxy group blockade dimethylsiloxane oligomer [of viscosity 60 mPa-s], and specific surface area [of 200 m] ²/g into the kneader mixer and became bottom homogeneity of heating, and the silicone rubber base was produced. To 100 copies of this silicone rubber base, subsequently, 0.5 copy of P-methylbenzoyl peroxide, 1.0 copy of dicumyl peroxide, 1.0 copy of silicone resin hollow granular material obtained by the reference example 1, 0.5 copy of distilled water and 0.5 copy of azodicarbonamide system organic blowing agent (trade name BINIHORUAK#2) with a decomposition temperature of 122 ** were added, it mulled uniformly on 2 rolls, and the silicone rubber sponge plasticity constituent was obtained. After making this constituent into a 5-mm-thick sheet shaped, put in a 250 ** heating furnace, and heat for 10 minutes, it was made to harden, and the silicone rubber sponge sheet was obtained. When the foaming cell of this silicone rubber sponge sheet was observed, the foaming cell was almost uniform and the size of that cell was 0.1-0.4 mm in diameter.

[0054]

[Comparative example 1] In the working example 1, the silicone rubber sponge plasticity constituent was obtained like the working example 1 except not having added a silicone resin hollow granular material. After using this constituent as 5-mm-thick sheet-shaped mold goods, put into a 250 ** heating furnace, and heat for 10 minutes, it was made to harden, and the silicone rubber sponge sheet was obtained. The foaming cell of this silicone rubber sponge sheet is uneven, and many foaming cells not less than 3 mm in diameter were also accepted.

[0055]

[Comparative example 2] After feeding into 1 axis extrusion machine of 65 mmphi the silicone rubber sponge plasticity constituent obtained by the comparative example 1 and extruding to tube shape, heat for 5 minutes, it was made to harden all over a 250 ** heating furnace, and the silicone rubber sponge tube was obtained. The foaming cell is uneven and many foaming cells not less than 3 mm in diameter were also accepted.

[0056]

[Comparative example 3] It is a rectangular parallelepiped whose form of a cavity is 10mmx40mmx80mm, The capacity taught 16 cm of silicone rubber sponge plasticity constituent ³ obtained by the comparative example 1 to the compression mold which is 32cm³, it heated for 15 minutes at 170 **, and the conductive silicone rubber sponge molded product was obtained. Although the outside of this silicone rubber sponge molded product was faithful to the cavity form of a metallic mold, that foaming cell is uneven and many foaming cells not less than 3 mm in diameter

were also accepted.

[0057]

[Comparative example 4] In the working example 1, the silicone rubber sponge plasticity constituent was obtained like the working example 1 except not having added distilled water. After using this constituent as 5-mm-thick sheet-shaped mold goods, put into a 250 °C heating furnace, and heat for 10 minutes, it was made to harden, and the silicone rubber sponge sheet was obtained. Foaming of this silicone rubber sponge sheet was not enough.

[0058]

[Comparative example 5] In the working example 4, the silicone rubber sponge plasticity constituent was obtained like the working example 4 except not having added a silicone resin hollow granular material. After making this constituent into a 5-mm-thick sheet shaped, it supplies to 250 °C oven, heat cure was carried out to it for 10 minutes, and the silicone rubber sponge sheet was obtained. The foaming cell of this silicone rubber sponge sheet is uneven, and many foaming cells not less than 3 mm in diameter were also accepted.

[0059]

[Comparative example 6] In the working example 4, the silicone rubber sponge plasticity constituent was obtained like the working example 4 except not having added distilled water. After using this constituent as 5-mm-thick sheet-shaped mold goods, put into a 250 °C heating furnace, and heat for 10 minutes, it was made to harden, and the silicone rubber sponge sheet was obtained. Foaming of this silicone rubber sponge sheet was not enough.

[0060]

[Comparative example 7] In the working example 6, the conductive silicone rubber sponge plasticity constituent was obtained like the working example 6 except not having added a silicone resin hollow granular material. After making this constituent into a 5-mm-thick sheet shaped, it supplies to 250 °C oven, heat cure was carried out to it for 10 minutes, and the conductive silicone rubber sponge sheet was obtained. The foaming cell of this conductive silicone rubber sponge sheet is uneven, and many foaming cells not less than 3 mm in diameter were also accepted.

[0061]

[Comparative example 8] In the working example 12, the silicone rubber sponge plasticity constituent was obtained like the working example 12 except not having added a silicone resin hollow granular material. After making this constituent into a 5-mm-thick sheet shaped, it supplies to 250 °C oven, heat cure was carried out to it for 10 minutes, and the silicone rubber sponge sheet was obtained. The foaming cell of this silicone rubber sponge sheet is uneven, and many foaming cells not less than 3 mm in diameter were also accepted.

[0062]

[Effect of the Invention] The silicone rubber sponge plasticity constituent of this invention, (A) Since it consists of an ingredient - (F) ingredient and (G) thermoplastics hollow granular material and (D) boiling point contain the liquefied compound higher than a room temperature and the (E) heat decomposition type blowing agent especially, Having [and] after hardening the feature that it can become silicone rubber sponge which has a uniform and detailed foaming cell, the manufacturing method of the silicone rubber sponge plasticity constituent of this invention has the feature that this silicone rubber sponge plasticity constituent can be manufactured efficiently. The silicone rubber sponge of this invention heats said silicone rubber sponge plasticity constituent, hardens, and it has the feature of having a uniform and detailed foaming cell since, The manufacturing method of the silicone rubber sponge of this invention has the feature that this silicone rubber sponge can be manufactured efficiently.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention]This invention relates to a silicone rubber sponge plasticity constituent, silicone rubber sponge, and those manufacturing methods. It is related with the silicone rubber sponge plasticity constituent which can serve as silicone rubber sponge which has a uniform and detailed foaming cell in detail, the silicone rubber sponge which has a uniform and detailed foaming cell, and those manufacturing methods.

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EFFECT OF THE INVENTION

[Effect of the Invention]The silicone rubber sponge plasticity constituent of this invention, (A) Since it consists of an ingredient – (F) ingredient and (C) thermoplastics hollow granular material and (D) boiling point contain the liquefied compound higher than a room temperature and the (E) heat decomposition type blowing agent especially, Having [and] after hardening the feature that it can become silicone rubber sponge which has a uniform and detailed foaming cell, the manufacturing method of the silicone rubber sponge plasticity constituent of this invention has the feature that this silicone rubber sponge plasticity constituent can be manufactured efficiently. The silicone rubber sponge of this invention heats said silicone rubber sponge plasticity constituent, hardens, and it has the feature of having a uniform and detailed foaming cell since, The manufacturing method of the silicone rubber sponge of this invention has the feature that this silicone rubber sponge can be manufactured efficiently.

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TECHNICAL PROBLEM

[Description of the Prior Art]Conventionally, the silicone rubber sponge to which silicone rubber was made to add and carry out foam curing of the foaming agent is known. This silicone rubber sponge is excellent in heat resistance and weatherability, and since it is lightweight, it is used for the use broad as the parts for cars, parts for OA equipment, etc., and the concrete target as various sealants, packing, a gasket, an O ring, roll covering material, etc. taking advantage of that characteristic.

[0003]As this silicone rubber sponge composition, For example, the silicone rubber sponge composition (refer to JP,H8-12888,A) which blended the thermal expansion nature microcapsule which expands at the temperature of 80-200 **, The silicone rubber sponge composition (refer to JP,2000-186210,A and JP,2000-309710,A) etc. which blended hollow powder with a mean particle diameter of 200 micrometers or less are proposed. However, in the silicone rubber sponge composition containing these hollow fillers, In order to obtain the sponge to which it fully foamed, it is necessary to blend a hollow filler in large quantities by a volume ratio to organopolysiloxane. There was a problem that cost cost dearly, combination of a hollow filler was difficult, or the characteristics, such as the heat resistance of silicone rubber sponge, were spoiled under the influence of the wallplate of the hollow filler to blend.

[0004]As a method of forming silicone sponge, using harmless and inexpensive water as a foaming agent, The compound which can harden an aqueous emulsion to the silicone sponge contained as a foaming agent (refer to JP,H6-20738,A), The buffer vibroisolating material made from silicone (refer to JP,H4-13738,A) etc. which contain hydrolytic drugs, such as sodium bicarbonate, as a foaming agent under water existence are proposed. However, the foaming cell of the silicone rubber sponge obtained by this method was not enough in uniformity or a detail, and it was difficult for it to satisfy the performance demanded as roll covering material.

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- 3.In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem]"This invention, (A) polyorganosiloxane crude rubber 100 weight section, (B) The liquefied compound 0.1 – ten weight sections in which inorganic filler 1 – 500 weight section, (C) thermoplastics hollow granular material 0.01 – 10 weight section, and (D) boiling point are higher than a room temperature, (E) heat decomposition type blowing agent 0.1 – 10 weight section, and (F) hardening agent (sufficient quantity to stiffen this constituent)

A silicone rubber sponge plasticity constituent characterized by a thing, ** and others," "Silicone rubber sponge which carries out heat cure of this silicone rubber sponge plasticity constituent", "Mix (A) polyorganosiloxane crude rubber and the (B) inorganic filler, and a silicone rubber base is manufactured, To this silicone rubber base, after an appropriate time (C) thermoplastics hollow granular material, (D) After the boiling point blends a liquefied compound higher than a room temperature and the (E) heat decomposition type blowing agent, (F) A manufacturing method of said silicone rubber sponge plasticity constituent blending a hardening agent", And it is related with "a manufacturing method of silicone rubber sponge making temperature more than softening temperature of thermoplastics of the (C) ingredient heat and harden this silicone rubber sponge plasticity constituent."

[0007]

[Mode for carrying out the invention]Silicone rubber sponge which carries out heat cure of a silicone rubber sponge plasticity constituent of this invention and this silicone rubber sponge plasticity constituent to below, and those manufacturing methods are explained in detail.

(A) Polyorganosiloxane crude rubber is the main ingredients of this invention constituent.

Although it is preferred that it is straight chain shape as for the molecular structure, it may be straight chain shape with branching in part.

Ranges of a weight average degree of polymerization for Motoshige are usually 1,000–20,000. (A) As a basis combined with a silicon atom in an ingredient, Alkyl groups, such as a methyl group, an ethyl group, a propyl group, a butyl group, and an octyl group; A phenyl group, Aryl groups, such as a tolyl group; substitution or unsubstituted monovalent hydrocarbon groups, such as alkyl halide groups, such as alkenyl-group; chloromethyl groups, such as a vinyl group, an allyl group, a butenyl group, a hexenyl group, and a heptenyl group, and a 3,3,3-trifluoropropyl group, are illustrated. It may have a hydroxyl group in molecular chain terminals etc. a desirable alkenyl group — a vinyl group — although it is subsequently a hexenyl group, a connecting position of this alkenyl group may not be limited, but may be molecular chain terminals, a chain side chain, or its both. As for the (A) ingredient, when using together a platinum system catalyst and polyorganosiloxane which has at least two silicon atom absorbed water matter atoms in one molecule as a (F) ingredient which carries out a postscript, it is preferred to have at least two alkenyl groups in one molecule. As for a basis combined with silicon atoms other than an alkenyl group, it is preferred that it is a methyl group.

[0008]As a desirable (A) ingredient, chain both-ends dimethylvinyl siloxy group blockade

polydimethyl siloxane crude rubber, Chain both-ends trimethylsiloxy group blockade polydimethyl siloxane crude rubber, Chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber, Chain both-ends dimethylvinyl siloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber, Chain both-ends dimethylhydroxy siloxy group blockade polydimethyl siloxane crude rubber, Chain both-ends dimethylhydroxy siloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber, Chain both-ends methylvinyl hydroxy siloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber, Chain both-ends dimethylhexenyl siloxy group blockade polydimethyl siloxane crude rubber, Chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylhexenyl siloxane copolymer crude rubber, chain both-ends dimethylhexenyl siloxy group blockade dimethylsiloxane methylhexenyl siloxane copolymer crude rubber, Chain both-ends dimethylvinyl siloxy group blockade dimethylsiloxane methylphenyl siloxane copolymer crude rubber, Chain both-ends dimethylhexenyl siloxy group blockade dimethylsiloxane methylphenyl siloxane copolymer crude rubber, Chain both-ends dimethylvinyl siloxy group blockade dimethylsiloxane methyl (3,3,3-trifluoropropyl) siloxane copolymer crude rubber, Two or more sorts of mixtures, chain both-ends dimethylhexenyl siloxy group blockade dimethylsiloxane methyl (3,3,3-trifluoropropyl) siloxane copolymer crude rubber and these polyorganosiloxane crude rubber, are illustrated.

[0009](B) As an inorganic filler, impalpable powder-like silica, such as dry process silica and wet process silica, Those surfaces Organochlorosilane, organoalkoxysilane, The reinforcement nature bulking agent illustrated by the impalpable powder-like silica etc. by which hydrophobing processing was carried out by hexa ORGANO disilazane, an organosiloxane oligomer, etc.; The end of quartz powder, A semi- reinforcement nature bulking agent thru/or increase-in-quantity bulking agents, such as diatomite, heavy calcium carbonate, precipitated calcium carbonate, magnesium oxide, silicic-acid calcium, mica, an aluminum oxide, and aluminium hydroxide, are illustrated. Since combination for the (A) ingredient will become difficult if too large, the loadings for Motoshige are 1 - 500 weight section to (A) ingredient 100 weight section, a reinforcement nature bulking agent has 1 - 100 preferred weight section, and a semi- reinforcement nature bulking agent thru/or an increase-in-quantity nature bulking agent have 1 - 300 preferred weight section.

[0010]It does not interfere, unless the purpose of this invention is spoiled, even if it chooses a conductive bulking agent as a (B) ingredient, in order to give conductivity to a silicone rubber sponge composition. As this conductive bulking agent, carbon system conducting agent; gold, such as carbon black, carbon fiber, and graphite, Metal-powder; conductive zinc oxides, such as silver and nickel, conductive titanium oxide, a conductive aluminum oxide; the conductive bulking agent which carried out electric conduction coating treatment to the various filler surfaces on the filler surface, such as carrying out metal plating processing, is illustrated. Even if it uses these conductivity bulking agent together with an inorganic filler and uses it alone, it does not interfere, and even if it uses together two or more kinds of conductive fillers, unless the purpose of this invention is spoiled, it does not interfere. As for especially the (B) ingredient, since good conductivity is obtained by a little addition, it is preferred that it is carbon black. Although what is usually regularly used by the conductive rubber constituent can be used as desirable carbon black, in order to avoid hardening inhibition of this invention constituent, it is preferred that it is carbon black of pH six to 10 range manufactured from the low-sulfur raw material. As for the loadings of these conductive bulking agents, it is preferred to be 1 - 200 weight section and to consider it as 5-100 copies especially to (A) ingredient 100 weight section. This is because sponge may be hard to be obtained if conductivity is obtained as it is less than the minimum of a mentioned range, it may not be and the maximum of a mentioned range is surpassed.

[0011]While (C) thermoplastics hollow powder used for this invention becomes a core of the foaming cell formed into the silicone rubber sponge produced by making carry out heat cure of this invention constituent, it serves to make the size of the foaming cell uniform. This (C) ingredient is hollow powder which contains a gas in the inside by using thermoplastics as a coat. Here, as desirable

thermoplastics, silicone resin, an acrylic resin, and polycarbonate resin are illustrated. As for the softening temperature of this thermoplastics, 40–200 °C is preferred, and its 60–180 °C is more preferred. As a gas included by this hollow granular material, inactive gas, such as air or nitrogen gas, and gaseous helium, is preferred. (C) The size of an ingredient has a preferred range in which the mean particle diameter is 0.1–500 micrometers, and its range which is 1–50 micrometers is more preferred. This (C) ingredient sprays the dispersion liquid of the thermoplastics and water which dissolved in the solvent in a heat style from a spray nozzle, for example, and it is manufactured by carrying out disintegration of the thermoplastics while dispersing an organic solvent. The loadings for Motoshige are 0.01 – 10 weight section to (A) ingredient 100 weight section. It is preferred that it is 0.1 to 5 weight section.

[0012](D) When the liquid which has the boiling point higher than a room temperature carries out heat cure of this invention constituent and forms silicone rubber sponge, in order to volatilize, to carry out the work as a foaming agent and to form a uniform and detailed foaming cell with the (C) ingredient and the (E) ingredient mentioned later, it is an ingredient made indispensable. This is because this liquid volatilizes and good silicone rubber sponge may not no longer be obtained, while keeping this invention constituent if the boiling point is lower than a room temperature.

Corresponding to the formation method and its formation condition of silicone rubber sponge as a (D) ingredient, Although what is necessary is just to select what has the suitable boiling point higher than a room temperature, it is preferred that it is a liquid which generally has the boiling point of the range of 25–200 °C, and it is more preferred that it is a liquid which has the boiling point of the range which is 50–180 °C.

[0013]It is necessary to dissolve the wallplate of the (C) ingredient during storage of this invention constituent or, when carrying out heat cure of this invention constituent and forming conductive silicone rubber sponge, heating does not need to decompose, or the (D) ingredient does not need to be accompanied by a chemical reaction with other ingredients.

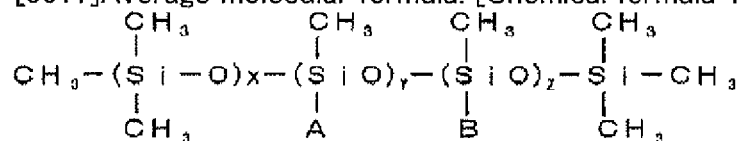
[0014]As this (D) ingredient, water; methanol, ethanol, 1-propanol, Alcohols, such as cyclohexanol; Ethylene glycol monoethyl ether, Ethylene glycol derivatives, such as ethylene glycol monoethyl ether acetate; Hexamethyl cyclotrisiloxane, annular dimethylsiloxane oligomer [, such as octamethylcyclotetrasiloxane,]; -- chain both-ends trimethylsiloxy group blockade dimethylsiloxane oligomer; -- chain both-ends dimethylhydroxy siloxy group blockade dimethylsiloxane oligomer. And two or more sorts of these mixtures are illustrated. Water is the most preferred in these and, subsequently annular dimethylsiloxane oligomer is preferred. Water with purity high as water called pure water, purified water, ion exchange water, etc. is preferred.

[0015](D) Although an ingredient may be directly blended with the silicone rubber base which mixes the (A) ingredient and the (B) ingredient, it aims at improvement in the handling nature of the (D) ingredient, or improvement in the dispersibility to a silicone rubber base, (D) Even if it blends an ingredient with a silicone rubber base with the form of a mixture with adsorption granular materials, such as thickening agents, such as silica powder, and porous powder, unless the purpose of this invention is spoiled, don't interfere. When the (D) ingredient is water, blending a mixture and silicone oil with water-soluble silicone in the form of the emulsion of the water-in-oil type made into an oil reservoir does not interfere, either, unless the purpose of this invention is spoiled.

[0016](D) When choosing water as an ingredient and blending with a silicone rubber base as a mixture with water-soluble silicone, the water-soluble silicone should just be silicone which can be dissolved in water, and the kind in particular is not limited. Although the loadings in particular to the water of water-soluble silicone are not limited, it is preferred that it is 1 to 80 weight %, and it is especially preferred that it is 5 to 70 weight %. As silicone which can be dissolved in this water, although polyoxyalkylene modified silicone oil, amino alkyl-group content silicone oil, amide group content silicone oil, a carbinol group content siloxane oligomer, etc. are mentioned, Polyoxyalkylene modified silicone oil is preferred also in these. The organopolysiloxane which has a polyoxyalkylene

group as this polyoxyalkylene modified silicone oil at a side chain or an end as shown with the following average molecular formula is illustrated.

[0017]Average molecular formula: [Chemical formula 1]

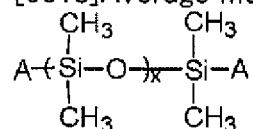


{x and y are one or more integers among a formula, and z is 0 or one or more integers. A is general formula: $-(\text{CH}_2)_a - \text{O} - (\text{C}_2\text{H}_4\text{O})_p (\text{C}_3\text{H}_6\text{O})_q \text{R}$ (as for the integer of 1-3, and p, one or more integers and q of a are 0 or one or more integers among a formula.).

R is an alkyl group with 1-4 carbon atoms, such as a hydrogen atom or a methyl group, an ethyl group, and a propyl group. It is an organic group shown and B is an organic group shown by general formula: $-(\text{CH}_2)_n - \text{CH}_3$ (n is an integer of 7-23 among a formula.).

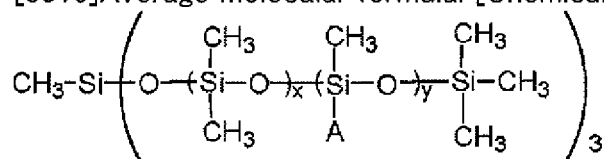
}

[0018]Average molecular formula: [Chemical formula 2]



(x and A are the same as the above among a formula.)

[0019]Average molecular formula: [Chemical formula 3]



(x, y, and A are the same as the above among a formula.)

[0020]In order for this polyoxyalkylene modified silicone oil to acquire good water solubility, a polyoxyalkylene portion is a polyoxyethylene or an oxyethylene oxypropylene copolymer, and that in which the content in a molecule is 50 weight % or more is preferred.

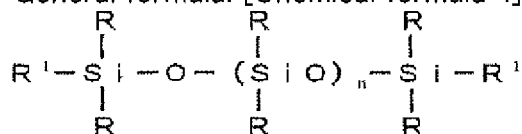
[0021] Water is chosen as a (D) ingredient, and when blending with a silicone rubber base as a water-in-oil type emulsion which made silicone oil the oil reservoir, this water-in-oil type emulsion is easily manufactured by distributing water in silicone oil with a surface-active agent. Although the content in particular of the water in this water-in-oil type emulsion is not limited, it is preferred that it is 1 to 80 weight %, and it is especially preferred that it is 20 to 70 weight %.

[0022][0022]. as for Thilly who becomes an oil reservoir, NOIRU makes JIORUGANO siloxane units a main skeleton -- oligomer -- it comes out.

What is necessary is to be Maher, to present the shape of liquid and for especially the kind just to be.

The following diorganopolysiloxane is illustrated as an example of representation of this silicone oil.

General formula: [Chemical formula 4]

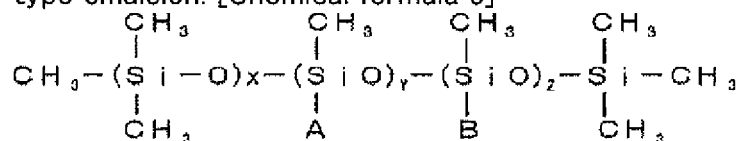


(R is a monovalent hydrocarbon group or an alkyl halide group among a formula.)

R¹ is R or a hydroxyl group.

As a monovalent hydrocarbon group, a methyl group, an ethyl group, a propyl group, a butyl group, Aralkyl groups, such as cycloalkyl group; beta-phenylethyl groups, such as alkenyl-group; cyclohexyl groups, such as alkyl-group; vinyl groups, such as a pentyl group and a hexyl group, an allyl group, and a hexenyl group; Aryl groups, such as a phenyl group, etc. are illustrated. As an alkyl halide group, 3-chloropropyl group and a 3,3,3-trichloropropyl group are illustrated. An alkyl group, especially a methyl group are preferred also in these. n is zero or more integers. It is expressed, and the viscosity at 25 °C is within the limits of 1 - 100,000 mPa·s, and is within the limits of 10 - 100,000 mPa·s preferably.

[0023] As a surface-active agent, what is necessary is just a surface-active agent which can form a water-in-oil type emulsion, and if hardening inhibition is not caused, the kind in particular will not be limited. Diorganopolysiloxane, a general formula which have a polyoxyalkylene group in a side chain as shown with a following general formula as a surface-active agent for forming this water-in-oil-type emulsion: [Chemical formula 5]



(x, y, z, A, and B are as aforementioned among a formula.) -- the polydimethyl siloxane which has a polyoxyalkylene group shown by the above-mentioned formula A in molecular chain terminals.

Polyoxyethylene sorbitan fatty acid ester, polyoxyethylene sorbitol fatty acid ester, The mixture of non-ion system surface-active agents, such as polyethylene glycol fatty acid ester, polyoxyethylene alkyl ether, and polyoxyethylene alkyl phenyl ether, and the above-mentioned polyoxyalkylene group content organopolysiloxane and the above-mentioned non-ion system surface-active agent is illustrated. (D) The loadings of an ingredient are 0.01 - 10 weight section to (A) ingredient 100 weight section. This is because it stops fully working as a foaming agent when the cell of the silicone sponge which will be fabricated if the maximum of a mentioned range is exceeded becomes uneven easily and less than the minimum of a mentioned range becomes.

[0024] (E) When a heat decomposition type blowing agent carries out heat cure of this invention constituent and forms silicone rubber sponge, in order to serve to assist the (D) ingredient and to form a uniform and detailed foaming cell with the (C) ingredient and the (D) ingredient, it is an ingredient made indispensable. As this heat decomposition type blowing agent, the conventionally publicly known inorganic foaming agent and/or organic blowing agent which are used for the silicone rubber sponge composition can be used.

[0025] As an inorganic foaming agent, sodium bicarbonate, potassium bicarbonate, sodium borohydride, calcium azido, etc. are illustrated. Sodium bicarbonate is especially preferred.

[0026] As an organic blowing agent, azobisisobutyronitrile, 2, 2'-azobis (2,4-dimethylvaleronitrile), Azo compound; N,N'-dinitrosopentamethylenetetramines, such as dimethyl- 2,2'-azobisisobutyrate and an azodicarbonamide, Nitroso compounds, such as N,N'-dimethyl- N,N'-dinitroso terephthalamide; p-tosyl hydrazide, Sulfonylhydrazide compound; 2-propenoic acid hydrazide, such as 4,4'-oxybis benzene sulfonylhydrazide and diphenylsulfone-3,3'-disulfonylhydrazide, Carbonyl hydrazine compounds, such as acetylhydrazine; diazido compounds, such as 4,4'-diazide diphenyl, 4,4'-diazido benzophenone, and 2,5-diazido toluene, etc. are illustrated. The amount of Motoshige may use together and use one kind of heat decomposition type blowing agents [two or more kinds of].

[0027] (E) The loadings of an ingredient are 0.1 - 10 weight section to (A) ingredient 100 weight section, and it is preferred that it is 0.1 - 1.0 weight section. This is because hardening inhibition may be caused or the heat resistance of the silicone rubber sponge obtained may get worse, when the silicone rubber sponge to which it fully foamed is not obtained in case of less than the minimum of a mentioned range but the maximum of a mentioned range is exceeded.

[0028](F) A hardening agent is an ingredient for stiffening this invention constituent, and the kind in particular is not limited. Organic peroxide is mentioned as a typical hardening agent. As such organic peroxide, benzoyl peroxide, di-*t*-butyl peroxide, 2,5-dimethyl- 2,5-di(*tert*-butylperoxy) hexane, Bis (ortho-methylbenzoyl) peroxide, bis(meta-methylbenzoyl) peroxide, Dimethylbenzoyl peroxide, such as monomethylbenzoyl peroxide, such as bis(****- methylbenzoyl)peroxide, and bis(2,4-dimethylbenzoyl)peroxide, bis(2,4,6-trimethyl benzoyl)peroxide **, etc. are illustrated. The loadings for Motoshige are 0.1 – 10 weight section to mixture 100 weight section of a (A) ingredient – (D) ingredient.

[0029]In being what has the alkenyl group that (A) polyorganosiloxane crude rubber is represented with a vinyl group, in [at least two] one molecule, Hardening by an addition hardening reaction is possible for this invention constituent, and into one molecule, it can use together polyorganosiloxane and a platinum system catalyst containing at least two silicon atom absorbed water matter atoms, and can use them as a hardening agent. Since the concomitant use of this polyorganosiloxane and a platinum system catalyst can change hardenability arbitrarily, it is preferred as a hardening agent of this invention constituent.

[0030]As such polyorganosiloxane, A chain both-ends trimethylsiloxy group blockade polymethyl hydrogen siloxane, A chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane copolymer, A chain both-ends dimethyl hydrogen siloxy group blockade dimethylsiloxane methylhydrogensiloxane copolymer, An annular dimethylsiloxane methylhydrogensiloxane copolymer, Siloxane units expressed per annular polymethyl hydrogen siloxane and formula:(CH₃)₃SiO_{1/2}, A formula : (CH₃) Organopolysiloxane which consists of siloxane units shown by siloxane-units [which are expressed per $\frac{1}{2}$ HSiO_{1/2}], and formula:SiO_{4/2}, A formula : (CH₃) Siloxane units expressed per organopolysiloxane [which consists of siloxane units shown per siloxane-units / which are expressed per $\frac{1}{2}$ HSiO_{1/2} /, and formula:CH₃SiO_{3/2}], and formula:(CH₃) $\frac{1}{2}$ HSiO_{1/2}, The formula : (CH₃) $\frac{2}{2}$ SiO₂ / $\frac{2}{2}$ unit, and a formula : Organopolysiloxane which consists of siloxane units shown per CH₃SiO_{3/2}, A chain both-ends dimethyl hydrogen siloxy group blockade polydimethyl siloxane, A chain both-ends dimethyl hydrogen siloxy group blockade dimethylsiloxane methylphenyl siloxane copolymer, Two or more sorts of mixtures, chain both-ends dimethyl hydrogen siloxy group blockade dimethylsiloxane methyl (3,3,3-trifluoropropyl) siloxanes and such polyorganosiloxanes, are illustrated. Although viscosity in particular at 25 ** of this polyorganosiloxane is not limited, it is preferred that it is the range of 2 – 100000 mPa-s. The addition needs to be quantity that a ratio of the number of sum total mols of a silicon atom absorbed water matter atom in this polyorganosiloxane and the number of sum total mols of an alkenyl group in the (A) ingredient becomes – (0.5:1) (20:1).

[0031]As a platinum system catalyst, in this case, the denaturing alcohol thing of particle platinum, chloroplatinic acid, and chloroplatinic acid, Chelate compound of platinum, platinum and the complex of diketone, chloroplatinic acid and the coordinated complex of olefins, The complex of chloroplatinic acid and an alkenyl siloxane, and these Alumina, The thing which carriers, such as silica and carbon black, were made to support is illustrated, and also in these, since activity is high as a catalyst for a hydrosilylation reaction, the complex of chloroplatinic acid and an alkenyl siloxane is preferred, A platinum alkenyl siloxane complex which is indicated by especially JP,S42-22924,B is preferred. The spherical-particles catalyst which comprises thermoplastics which uses a platinum system catalyst as a platinum metal atom, and contains it 0.01weight % or more can also be used. As for the quantity of the platinum metal in a platinum system catalyst, it is preferred that it is within the limits of 0.01 – 500 weight section to (A) ingredient 1 million weight section, and it is especially preferred that this is within the limits of 0.1 – 100 weight section.

[0032]In using together a platinum system catalyst and the polyorganosiloxane which has at least two silicon atom absorbed water matter atoms in one molecule as a (F) ingredient, In order to raise

the handling workability and storage stability of this invention constituent, a 2-methyl-3-butyn-2-ol, A 2-phenyl-3-butyn-2-ol, 3,5-dimethyl-1-hexyn-3-ol, Acetylene series compound; 3,5-dimethyl-1-hexene-1-yne, such as 1-ethynyl-1-cyclohexanol, 1,5-hexadiyne, and 1,6-heptadiyne, Ene-yne compound; 1,3-divinyl tetramethyl disiloxane, such as 3-ethyl-3-butene-1-yne and 3-phenyl-3-butene-1-yne, 1, 3, 5, 7-tetravinyl tetramethyl cyclotetrasiloxane, alkenyl siloxane oligomer [, such as a 1,3-divinyl-1,3-diphenyl dimethyldi siloxane,]; -- ethynyl group content silicon compound [, such as methyltris (3-methyl-1-butyne-3-oxy) Silang,]; -- tributylamine. Phosphorus content compounds, such as nitrogen containing compound; triphenyl phosphine, such as tetramethylethylenediamine and benzotriazol; In addition to this, a sulfur content compound, It is preferred to blend hardening depressants, such as a hydro-peroxy compound, maleic acid derivatives, and two or more sorts of these mixtures.

[0033][0033]. Three or less weight sections may be sufficient as loadings of ** to (A) ingredient 100 weight section, and these ***** are usually 0.00.

It is a quantity part and is 0.01-1 preferably.

A desirable hardening depressant is the acetylene series compound which was illustrated above, and these demonstrate sufficient preservation stability of a constituent, and quick hardenability with sufficient balance.

[0034]As arbitrary ingredients, in addition, pyrogenic silica, aluminium hydroxide, an aluminum oxide, The end of quartz powder, diatomite, an aluminosilicate, heavy calcium carbonate, precipitated calcium carbonate, Heat-resistant agents, such as paints; cerium oxide, such as inorganic filler; iron oxide, such as magnesium oxide, silicic-acid calcium, and mica, and a titanium dioxide, and hydroxylation cerium; fire retardant, such as manganese carbonate, zinc carbonate, and fumed titanium dioxide, may be contained. These inorganic fillers may use what could use an unsettled thing and was beforehand processed by a finishing agent.

[0035]Furthermore to this invention constituent, a chain both-ends trimethylsiloxy group blockade polydimethyl siloxane, A chain both-ends dimethylhydroxy siloxy group blockade polydimethyl siloxane, A chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylphenyl siloxane copolymer, A chain both-ends trimethylsiloxy group blockade dimethylsiloxane diphenyl siloxane copolymer, A chain both-ends dimethylhydroxy siloxy group blockade dimethylsiloxane methylphenyl siloxane copolymer, A chain both-ends trimethylsiloxy group blockade dimethylsiloxane methyl (3,3,3-trifluoropropyl) siloxane copolymer etc., Liquefied polyorganosiloxane which does not have a silicon atom joint alkenyl group and a silicon atom absorbed water matter atom; Silicone rubber powder, Silicone powdered additive agents, such as silicone resin powder; mold lubricant; adhesion promoters, such as stearic acid, calcium stearate, zinc stearate, and cerium stearate, etc. may be contained.

[0036] Although this invention constituent can be easily manufactured the above (A) ingredient - (F) ingredients or by adding other ingredients if needed further and mixing uniformly, (B) When it contains a reinforcement nature bulking agent as an ingredient, after mulling the finishing agent of a reinforcement nature bulking agent under heating the (A) ingredient, this reinforcement nature bulking agent, and if needed and manufacturing a silicone rubber base, mixing with other ingredients is preferred. As a manufacturing installation, mixed equipment or kneading apparatus, such as a kneader mixer and a continuation extruding kneading machine, are illustrated.

[0037]What is necessary is to heat this invention constituent to the temperature more than the softening temperature of the thermoplastics which constitutes the (C) ingredient, and just to stiffen it, in order to manufacture silicone rubber sponge from this invention constituent. In that case, it is hardened foaming to this invention constituent, and forms silicone rubber sponge. Since this invention constituent can form good silicone rubber sponge also in extrusion molding and the pressing which used the metallic mold, The silicone rubber sponge of various form, such as a sheet shaped, ring shape, the shape of string, and tube shape, can be fabricated, and there is the feature of being suitable also for production of a composite molding thing with metal or other organic resin.

The silicone rubber sponge obtained in this way has a uniform and detailed foaming cell, for example, is useful as the gasket for airtight maintenance of a structural component, a fire-resistant gasket, a sealant, an O ring, a cushioning material, a surface coating material of a copying machine roll, etc.

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EXAMPLE

[Working example]Next, an working example and a reference example explain this invention. There is a weight section among an working example with a part, and viscosity is a value at 25 **.

[0039]

[The reference example 1] It comprises methyl siloxane units and methylphenyl siloxane units, The mole ratio made a solution (30 weight % of the amounts of solid content) which dissolved in dichloromethane silicone resin (80 ** of softening temperatures, specific gravity 1.20) which is 22:78 100-cc the amount of supply for /, carried out liquid transport of the pure water into a dynamic mixer by 25-cc the amount of supply for /, was mixed, and considered it as a water dispersion. Subsequently, it sprayed continuously in a spray dryer which made this water dispersion a nitrogen gas air current using 2 hydraulic nozzles. Heat style temperature of nitrogen gas at this time was 70 **, and pressures were 0.05MPa. An obtained silicone resin hollow granular material was immersed in solution which consists of 100 copies of pure water, and one copy of nonionic surface active agent (ethyleneoxide addition of trimethyl nonanol) for 24 hours, and a silicone resin hollow granular material which floated was classified and caught. Mean particle diameter is 40 micrometers, average thickness of the coat is 4 micrometers, and an obtained silicone resin hollow granular material had included nitrogen gas to the inside.

[0040]

[Reference example 2] an average molecular formula -- $\text{Me}_3\text{SiO}-(\text{Me}_2\text{SiO})_7-\text{Me}$ is a methyl group among a $7-(\text{MeR}^2\text{SiO})_3-\text{SiMe}_3$ [type, and R^2 shows the basis expressed with formula: $-(\text{CH}_2)_2-\text{O}-(\text{C}_2\text{H}_4\text{O})_{12}-\text{H}$. 40 copies of water-soluble polyoxyalkylene modified silicone oil and 60 copies of ion exchange water of viscosity 400 mPa-s which are shown by] were uniformly mixed in the flask, and solution (the following, the solution A) was prepared.

[0041]

[Reference example 3] an average molecular formula -- $\text{Me}_3\text{SiO}-(\text{Me}_2\text{SiO})_7-\text{Me}$ and R^2 are the same as that of the above among a $0-(\text{MeR}^2\text{SiO})_3-\text{SiMe}_3$ [type. 50 copies of chain both-ends trimethylsiloxy group blockade polydimethyl siloxanes of ten copies of polyoxyalkylene modified silicone oil of viscosity 1600 mPa-s and viscosity 100 mPa-s shown by] were put into the flask, and were stirred strongly. Subsequently, the water-in-oil type emulsion which made the oil reservoir the chain both-ends trimethylsiloxy group blockade polydimethyl siloxane of viscosity 100 mPa-s was prepared by adding 40 copies of ion exchange water gradually to this, and mixing to it.

[0042]

[Work example 1]100 copies of chain both-ends dimethylvinyl siloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber which consists of 99.85 mol of dimethylsiloxane unit %, and 0.15 mol of methylvinyl siloxane-units % (degree of polymerization 3000), It mulled until it put 40 copies of dry process silica of specific surface area [of 200 m] ²/g by ten copies of chain both-

ends dimethylhydroxy siloxy group blockade dimethylsiloxane oligomer of viscosity 60 mPa-s, and a BET adsorption method into the kneader mixer and became bottom homogeneity of heating, and the silicone rubber base was produced. Subsequently, 100 copies of this silicone rubber base is received, 1.0 copy (this chain both-ends trimethylsiloxy group blockade dimethylsiloxane methyl hydrogen SHIROKI.) of chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane copolymer of 25 mPa-s (0.8 weight % of silicon atom absorbed water matter atom content) The quantity from which the ratio of the number of mols of the silicon atom absorbed water matter atom in the Sun copolymer and the number of mols of the silicon atom joint vinyl group in the above-mentioned vinyl group content polydyorganosiloxane crude rubber is set to 4.9, As a hydrosilylation reaction inhibitor, 0.015 copy of 1-ethynyl-1-cyclohexanol, The complex (0.6 weight % of platinum content) of chloroplatinic acid and tetramethyl divinyl disiloxane 0.06 copy, 1.0 copy of silicone resin hollow granular material, 0.5 copy of distilled water, and 0.5 copy of sodium bicarbonate which were obtained by the reference example 1 were added, it mulled uniformly on 2 rolls, and the silicone rubber sponge plasticity constituent was obtained. After making this constituent into a 5-mm-thick sheet shaped, put in a 250 ** heating furnace, and heat for 10 minutes, it was made to harden, and the silicone rubber sponge sheet was obtained. When the foaming cell of this silicone rubber sponge sheet was observed, the foaming cell was almost uniform and the size of that cell was 0.1-0.4 mm in diameter.

[0043]

[Work example 2] After feeding into 1 axis extrusion machine of 65 mmphi the silicone rubber sponge plasticity constituent obtained in working example 1 and extruding as tube shape mold goods, it heated for 4 minutes all over a 250 ** heating furnace, and the silicone rubber sponge tube was obtained. The foaming cell of this silicone rubber sponge tube was almost uniform, and the size of that foaming cell was 0.1-0.5 mm in diameter.

[0044]

[Work example 3]The form of the cavity taught 16 cm of 10 mmx constituent [which was obtained in working example 1 / silicone rubber sponge plasticity] ³ to the compression mold in which it is a rectangular parallelepiped which are 40 mm x 80 mm, and the capacity is 32cm³, it heated for 15 minutes at 170 **, and the silicone rubber sponge molded product was obtained. The outside of this silicone rubber sponge molded product was faithful to the cavity form of a metallic mold, and the size of that foaming cell was 0.1-0.4 mm in diameter, and was almost uniform.

[0045]

[Work example 4]100 copies of chain both-ends dimethylvinyl siloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber which consists of 99.85 mol of dimethylsiloxane unit %, and 0.15 mol of methylvinyl siloxane-units % (degree of polymerization 3000), It mulled until it put 40 copies of dry process silica of ten copies of chain both-ends dimethylhydroxy siloxy group blockade dimethylsiloxane oligomer [of viscosity 60 mPa-s], and specific surface area [of 200 m] ²/g into the kneader mixer and became bottom homogeneity of heating, and the silicone rubber base was produced. Subsequently, 100 copies of this silicone rubber base is received, 1.0 copy (this chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane.) of trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane copolymer of 25 mPa-s (0.8 weight % of silicon atom absorbed water matter atom content) The quantity from which the ratio of the number of mols of the silicon atom absorbed water matter atom in a copolymer and the number of mols of the silicon atom joint vinyl group in the above-mentioned vinyl group content polydyorganosiloxane crude rubber is set to 4.9, As a hydrosilylation reaction inhibitor, 0.015 copy of 1-ethynyl-1-cyclohexanol, The complex (0.6 weight % of platinum content) of chloroplatinic acid and tetramethyl divinyl disiloxane 0.06 copy, 1.0 copy of silicone resin hollow granular material, 0.5 copy of distilled water which were obtained by the reference example 1, 0.5 copy of azodicarbonamide system organic blowing agent with a decomposition temperature of 122 ** (trade name

BINIHORUAK#2), 0.5 copy of 2, 5-dimethyl- 2, and 5-JI (tertiary butyl peroxy) hexane were added as a hardening auxiliary agent, it mulled uniformly on 2 rolls, and the silicone rubber sponge plasticity constituent was obtained. After making this constituent into a 5-mm-thick sheet shaped, put in a 250 ** heating furnace, and heat for 10 minutes, it was made to harden, and the silicone rubber sponge sheet was obtained. When the foaming cell of this silicone rubber sponge sheet was observed, the foaming cell was almost uniform and the size of that cell was 0.1–0.4 mm in diameter. [0046]

[Work example 5]The form of the cavity taught 10 cm of 10 mmx constituent [which was obtained in working example 4 / silicone rubber sponge plasticity] ³ to the compression mold in which it is a rectangular parallelepiped which are 40 mm x 80 mm, and the capacity is 32cm³, it heated for 15 minutes at 170 **, and the silicone rubber sponge molded product was obtained. The outside of this silicone rubber sponge molded product was faithful to the cavity form of a metallic mold, and the size of that foaming cell was 0.1–0.5 mm in diameter, and was almost uniform. [0047]

[Work example 6]100 copies of chain both-ends dimethylvinyl siloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber which consists of 99.85 mol of dimethylsiloxane unit %, and 0.15 mol of methylvinyl siloxane-units % (degree of polymerization 3000), It mulled until it put 20 copies of dry process silica of five copies of chain both-ends dimethylhydroxy siloxy group blockade dimethylsiloxane oligomer [of viscosity 60 mPa-s], and specific surface area [of 200 m] ²/g into the kneader mixer and became bottom homogeneity of heating, and the silicone rubber base was obtained. It mulled until it added 15 copies of acetylene black (DENKA black; made by DENKI KAGAKU KOGYO KABUSHIKI KAISHA) to 125 copies of this silicone rubber base and became uniform at the room temperature in it, and the conductive silicone rubber base was produced. Subsequently, 100 copies of this conductive silicone rubber base is received, 1.0 copy (this chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane.) of trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane copolymer of 25 mPa-s (0.8 weight % of silicon atom absorbed water matter atom content) The quantity from which the ratio of the number of mols of the silicon atom absorbed water matter atom in a copolymer and the number of mols of the silicon atom joint vinyl group in the above-mentioned vinyl group content polydyorganosiloxane crude rubber is set to 4.5, As a hydrosilylation reaction inhibitor, 0.015 copy of 1-ethynyl-1-cyclohexanol, The complex (0.6 weight % of platinum content) of chloroplatinic acid and tetramethyl divinyl disiloxane 0.06 copy, 1.0 copy of silicone resin hollow granular material, 0.5 copy of distilled water, and 0.5 copy of sodium bicarbonate which were obtained by the reference example 1 were added, it mulled uniformly on 2 rolls, and the conductive silicone rubber sponge plasticity constituent was obtained. After making this constituent into a 5-mm-thick sheet shaped, put in a 250 ** heating furnace, and heat for 10 minutes, it was made to harden, and the conductive silicone rubber sponge sheet was obtained. When the foaming cell of this conductive silicone rubber sponge sheet was observed, the foaming cell was almost uniform and the size of that cell was 0.1–0.4 mm in diameter. [0048]

[Work example 7]After feeding into 1 axis extrusion machine of 65 mmphi the conductive silicone rubber sponge plasticity constituent obtained in working example 6 and extruding as tube shape mold goods, it heated for 4 minutes all over a 250 ** heating furnace, and the conductive silicone rubber sponge tube was obtained. The foaming cell of this conductive silicone rubber sponge tube was almost uniform, and the size of that foaming cell was 0.1–0.5 mm in diameter. [0049]

[Work example 8]It is a rectangular parallelepiped whose form of a cavity is 10mmx40mmx80mm, The capacity taught 16 cm of conductive silicone rubber sponge plasticity constituent ³ obtained in working example 6 to the compression mold which is 32cm³, it heated for 15 minutes at 170 **, and

the conductive silicone rubber sponge molded product was obtained. The outside of this conductive silicone rubber sponge molded product was faithful to the cavity form of a metallic mold, and the size of that foaming cell was 0.1–0.4 mm in diameter, and was almost uniform.

[0050]

[Work example 9]In the working example 6, the conductive silicone rubber sponge plasticity constituent was obtained like the working example 6 except having added 1.0 copy of solution A which was changed into distilled water and produced by the reference example 2 to 100 copies of conductive silicone rubber bases. After making this constituent into a 5-mm-thick sheet shaped, it supplies to 250 °C oven, heat cure was carried out to it for 10 minutes, and the conductive silicone rubber sponge sheet was obtained. The foaming cell of this conductive silicone rubber sponge sheet was uniform, and the size of that foaming cell was 0.1–0.5 mm in diameter.

[0051]

[Work example 10]In the working example 6, the conductive silicone rubber sponge plasticity constituent was obtained like the working example 6 except having added 1.2 copies of water-in-oil type emulsions which were changed into distilled water and produced by the reference example 3 to 100 copies of conductive silicone rubber base compounds. After making this constituent into a 5-mm-thick sheet shaped, it supplies to 250 °C oven, heat cure was carried out to it for 10 minutes, and the conductive silicone rubber sponge sheet was obtained. The foaming cell of this conductive silicone rubber sponge sheet was uniform, and the size of that foaming cell was 0.1–0.5 mm in diameter.

[0052]

[Work example 11]100 copies of chain both-ends dimethylvinyl siloxy group blockade organopolysiloxane crude rubber which consists of 99.85 mol of dimethylsiloxane unit %, and 0.15 mol of methylvinyl siloxane-units % (degree of polymerization 3000), It mulled until it put five copies of chain both-ends dimethylhydroxy siloxy group blockade dimethylsiloxane oligomer of viscosity 60 mPa·s, and 40 copies of wet process silica of specific surface area [of 200 m²/g] into the kneader mixer and became bottom homogeneity of heating, and the silicone rubber base was produced. Subsequently, 100 copies of this silicone rubber base is received, 1.0 copy (this chain both-ends trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane.) of trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane copolymer of 25 mPa·s (0.8 weight % of silicon atom absorbed water matter atom content) The quantity from which the ratio of the number of mols of the silicon atom absorbed water matter atom in a copolymer and the number of mols of the silicon atom joint vinyl group in the above-mentioned vinyl group content polydyorganosiloxane crude rubber is set to 4.6, As a hydrosilylation reaction inhibitor, 0.015 copy of 1-ethynyl-1-cyclohexanol, The complex (0.6 weight % of platinum content) of chloroplatinic acid and tetramethyl divinyl disiloxane 0.06 copy, 1.0 copy of silicone resin hollow granular material, 0.5 copy of distilled water, and 0.5 copy of sodium bicarbonate which were obtained by the reference example 1 were added, it mulled uniformly on 2 rolls, and the silicone rubber sponge plasticity constituent was obtained. After making this constituent into a 5-mm-thick sheet shaped, put in a 250 °C heating furnace, and heat for 10 minutes, it was made to harden, and the silicone rubber sponge sheet was obtained. When the foaming cell of this silicone rubber sponge sheet was observed, the foaming cell was almost uniform and the size of that cell was 0.1–0.4 mm in average diameter.

[0053]

[Work example 12]100 copies of chain both-ends dimethylvinyl siloxy group blockade dimethylsiloxane methylvinyl siloxane copolymer crude rubber which consists of 99.85 mol of dimethylsiloxane unit %, and 0.15 mol of methylvinyl siloxane-units % (degree of polymerization 3000), It mulled until it put 40 copies of dry process silica of ten copies of chain both-ends dimethylhydroxy group blockade dimethylsiloxane oligomer [of viscosity 60 mPa·s], and specific surface area [of 200 m²/g] into a kneader mixer and became bottom homogeneity of heating, and

a silicone rubber base was produced. To 100 copies of this silicone rubber base, subsequently, 0.5 copy of P-methylbenzoyl peroxide, 1.0 copy of dicumyl peroxide, 1.0 copy of silicone resin hollow granular material obtained by the reference example 1, 0.5 copy of distilled water and 0.5 copy of azodicarbonamide system organic blowing agent (trade name BINIHORUAK#2) with a decomposition temperature of 122 ** were added, it mulled uniformly on 2 rolls, and a silicone rubber sponge plasticity constituent was obtained. After making this constituent into a 5-mm-thick sheet shaped, put in a 250 ** heating furnace, and heat for 10 minutes, it was made to harden, and a silicone rubber sponge sheet was obtained. When a foaming cell of this silicone rubber sponge sheet was observed, a foaming cell was almost uniform and a size of that cell was 0.1–0.4 mm in diameter.

[0054]

[Comparative example 1] In the working example 1, the silicone rubber sponge plasticity constituent was obtained like the working example 1 except not having added a silicone resin hollow granular material. After using this constituent as 5-mm-thick sheet-shaped mold goods, put into a 250 ** heating furnace, and heat for 10 minutes, it was made to harden, and the silicone rubber sponge sheet was obtained. The foaming cell of this silicone rubber sponge sheet is uneven, and many foaming cells not less than 3 mm in diameter were also accepted.

[0055]

[Comparative example 2] After feeding into 1 axis extrusion machine of 65 mmphi the silicone rubber sponge plasticity constituent obtained by the comparative example 1 and extruding to tube shape, heat for 5 minutes, it was made to harden all over a 250 ** heating furnace, and the silicone rubber sponge tube was obtained. The foaming cell is uneven and many foaming cells not less than 3 mm in diameter were also accepted.

[0056]

[Comparative example 3] It is a rectangular parallelepiped whose form of a cavity is 10mmx40mmx80mm, The capacity taught 16 cm of silicone rubber sponge plasticity constituent³ obtained by the comparative example 1 to the compression mold which is 32cm³, it heated for 15 minutes at 170 **, and the conductive silicone rubber sponge molded product was obtained. Although the outside of this silicone rubber sponge molded product was faithful to the cavity form of a metallic mold, that foaming cell is uneven and many foaming cells not less than 3 mm in diameter were also accepted.

[0057]

[Comparative example 4] In the working example 1, the silicone rubber sponge plasticity constituent was obtained like the working example 1 except not having added distilled water. After using this constituent as 5-mm-thick sheet-shaped mold goods, put into a 250 ** heating furnace, and heat for 10 minutes, it was made to harden, and the silicone rubber sponge sheet was obtained. Foaming of this silicone rubber sponge sheet was not enough.

[0058]

[Comparative example 5] In the working example 4, the silicone rubber sponge plasticity constituent was obtained like the working example 4 except not having added a silicone resin hollow granular material. After making this constituent into a 5-mm-thick sheet shaped, it supplies to 250 ** oven, heat cure was carried out to it for 10 minutes, and the silicone rubber sponge sheet was obtained. The foaming cell of this silicone rubber sponge sheet is uneven, and many foaming cells not less than 3 mm in diameter were also accepted.

[0059]

[Comparative example 6] In the working example 4, the silicone rubber sponge plasticity constituent was obtained like the working example 4 except not having added distilled water. After using this constituent as 5-mm-thick sheet-shaped mold goods, put into a 250 ** heating furnace, and heat for 10 minutes, it was made to harden, and the silicone rubber sponge sheet was obtained. Foaming of this silicone rubber sponge sheet was not enough.

[0060]

[Comparative example 7] In the working example 6, the conductive silicone rubber sponge plasticity constituent was obtained like the working example 6 except not having added a silicone resin hollow granular material. After making this constituent into a 5-mm-thick sheet shaped, it supplies to 250 ** oven, heat cure was carried out to it for 10 minutes, and the conductive silicone rubber sponge sheet was obtained. The foaming cell of this conductive silicone rubber sponge sheet is uneven, and many foaming cells not less than 3 mm in diameter were also accepted.

[0061]

[Comparative example 8] In the working example 12, the silicone rubber sponge plasticity constituent was obtained like the working example 12 except not having added a silicone resin hollow granular material. After making this constituent into a 5-mm-thick sheet shaped, it supplies to 250 ** oven, heat cure was carried out to it for 10 minutes, and the silicone rubber sponge sheet was obtained. The foaming cell of this silicone rubber sponge sheet is uneven, and many foaming cells not less than 3 mm in diameter were also accepted.

[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号
特開2003-96223
(P2003-96223A)

(43) 公開日 平成15年4月3日(2003.4.3)

(51) Int.Cl. ⁷	識別記号	F I	テーマコード*(参考)
C 0 8 J 9/04	1 0 3 CFH	C 0 8 J 9/04	1 0 3 4 F 0 7 4 CFH 4 J 0 0 2
	9/32		9/32
C 0 8 K 3/00		C 0 8 K 3/00	
	5/00		5/00

審査請求 未請求 請求項の数16 O L (全 12 頁) 最終頁に続く

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(54) 【発明の名称】 シリコーンゴムスポンジ形成性組成物、シリコーンゴムスポンジおよびそれらの製造方法

(57) 【要約】

【課題】 均一かつ微細な発泡セルを有する導電性シリコーンゴムスポンジとなり得るシリコーンゴムスポンジ形成性組成物および均一かつ微細な発泡セルを有するシリコーンゴムスポンジならびにそれらの製造方法を提供する。

【解決手段】 A) ポリオルガノシロキサン生ゴム100重量部、(B) 無機質充填剤1~500重量部、(C) 熱可塑性樹脂中空粉体0.01~10重量部、(D) 沸点が室温より高い液状化合物0.1~10重量部、

(E) 熱分解型発泡剤0.1~10重量部および(F) 硬化剤(本組成物を硬化させるに十分な量)からなることを特徴とする、シリコーンゴムスポンジ形成性組成物、該シリコーンゴムスポンジ形成性組成物を硬化して得られるシリコーンゴムスポンジならびにそれらの製造方法。

【特許請求の範囲】

- 【請求項1】 (A) ポリオルガノシロキサン生ゴム 100重量部、
 (B) 無機質充填剤 1～500重量部、
 (C) 熱可塑性樹脂中空粉体 0.01～10重量部、
 (D) 沸点が室温より高い液化化合物 0.1～10重量部、
 (E) 熱分解型発泡剤 0.1～10重量部
 および
 (F) 硬化剤(本組成物を硬化させるに十分な量)

からなることを特徴とする、シリコーンゴムスポンジ形成性組成物。

【請求項2】 (C) 成分が、軟化点が40℃～200℃である熱可塑性樹脂からなる外殻を有し、内部に気体を含有了ものである、請求項1記載のシリコーンゴムスポンジ形成性組成物。

【請求項3】 (C) 成分の外殻を構成する熱可塑性樹脂が、シリコーン樹脂、アクリル樹脂またはポリカーボネート樹脂である、請求項2記載のシリコーンゴムスポンジ形成性組成物。

【請求項4】 (D) 成分が、水である請求項1～3のいずれか1項記載のシリコーンゴムスポンジ形成性組成物。

【請求項5】 (E) 成分が、無機発泡剤である請求項1～4のいずれか1項記載のシリコーンゴムスポンジ形成性組成物。

【請求項6】 (E) 成分が、有機発泡剤である請求項1～4のいずれか1項記載のシリコーンゴムスポンジ形成性組成物。

【請求項7】 (A) 成分が少なくとも2個のケイ素原子結合アルケニル基を有するポリオルガノシロキサン生ゴムであり、(F) 成分が白金系触媒{(A)成分100万重量部に対して白金系触媒に含まれる白金金属が0.01～100重量部の範囲}および1分子中に少なくとも2個のケイ素原子結合水素原子を有するポリオルガノシロキサン{(A)成分中のケイ素原子結合アルケニル基のモル数に対する本ポリオルガノシロキサン中のケイ素原子結合水素原子のモル数との比が0.5～20となる量}からなる請求項1～6のいずれか1項記載のシリコーンゴムスポンジ形成性組成物。

【請求項8】 押出成形用である請求項1～7のいずれか1項記載のシリコーンゴムスポンジ形成性組成物。

【請求項9】 金型を用いた加圧成形用である請求項1～7のいずれか1項記載のシリコーンゴムスポンジ形成性組成物。

【請求項10】 (A) ポリオルガノシロキサン生ゴムと(B) 無機質充填剤を混合してシリコーンゴムベースを製造し、しかる後、該シリコーンゴムベースに(C) 熱可塑性樹脂中空粉体、(D) 沸点が室温より高い液化化合物および(E) 熱分解型発泡剤を配合した後、

(F) 硬化剤を配合することを特徴とする、請求項1記載のシリコーンゴムスポンジ形成性組成物の製造方法。

【請求項11】 請求項1～9のいずれか1項記載のシリコーンゴムスポンジ形成性組成物を加熱硬化してなるシリコーンゴムスポンジ。

【請求項12】 シリコーンゴムスポンジがシート状である請求項11に記載のシリコーンゴムスポンジ。

【請求項13】 シリコーンゴムスポンジがチューブ状またはひも状である請求項11に記載のシリコーンゴムスポンジ。

【請求項14】 シリコーンゴムスポンジがロールの被覆材である請求項11に記載のシリコーンゴムスポンジ。

【請求項15】 シリコーンゴムスポンジがガasketである請求項11に記載のシリコーンゴムスポンジ。

【請求項16】 請求項1～9のいずれか1項記載のシリコーンゴムスポンジ形成性組成物を、(C) 成分を構成する熱可塑性樹脂の軟化点以上の温度に加熱して硬化させることを特徴とするシリコーンゴムスポンジの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、シリコーンゴムスポンジ形成性組成物、シリコーンゴムスポンジおよびそれらの製造方法に関するものである。詳しくは、均一かつ微細な発泡セルを有するシリコーンゴムスポンジとなり得るシリコーンゴムスポンジ形成性組成物、均一かつ微細な発泡セルを有するシリコーンゴムスポンジおよびそれらの製造方法に関するものである。

【0002】

【従来の技術及び発明が解決しようとする課題】従来、シリコーンゴムに発泡剤を加えて発泡硬化させたシリコーンゴムスポンジは知られている。このシリコーンゴムスポンジは耐熱性、耐候性に優れ、軽量であるので、その特性を活かして自動車用部品やOA機器用部品等として幅広い用途、具体的には各種シール材、パッキング、ガasket、Oリング、ロール被覆材などとして使用されている。

【0003】かかるシリコーンゴムスポンジ組成物としては、例えば、80～200℃の温度で膨張する熱膨張性マイクロカプセルを配合したシリコーンゴムスポンジ組成物(特開平8-12888号公報参照)や、平均粒子径200μm以下の中空粉末を配合したシリコーンゴムスポンジ組成物(特開2000-186210号公報

および特開2000-309710号公報参照)などが提案されている。しかし、これらの中空フィラーを含有するシリコーンゴムスポンジ組成物においては、十分に発泡したスポンジを得るためには、オルガノポリシロキサンに対して体積比で大量に中空フィラーを配合する必要がある、コストが高つくいたり、中空フィラーの配合が困難であったり、配合する中空フィラーの壁材の影響でシリコーンゴムスポンジの耐熱性などの特性が損なわれたりするという問題があった。

【0004】また、無害で安価な水を発泡剤として用いてシリコーンスポンジを形成する方法としては、水性エマルジョンを発泡剤として含有するシリコーンスポンジに硬化可能な配合物(特開平6-20738号公報参照)、水存在下に炭酸水素ナトリウムなどの加水分解性薬剤を発泡剤として含有するシリコーン製緩衝防振材

- 「(A) ポリオルガノシロキサン生ゴム
- (B) 無機質充填剤
- (C) 熱可塑性樹脂中空粉体
- (D) 沸点が室温より高い液化化合物
- (E) 熱分解型発泡剤

および

- (F) 硬化剤(本組成物を硬化させるに十分な量)

からなることを特徴とするシリコーンゴムスポンジ形成性組成物」、「該シリコーンゴムスポンジ形成性組成物を加熱硬化してなるシリコーンゴムスポンジ」、

「(A) ポリオルガノシロキサン生ゴムと(B) 無機質充填剤を混合してシリコーンゴムベースを製造し、しかる後、該シリコーンゴムベースに(C) 熱可塑性樹脂中空粉体、(D) 沸点が室温より高い液化化合物および(E) 熱分解型発泡剤を配合した後、(F) 硬化剤を配合することを特徴とする、前記シリコーンゴムスポンジ形成性組成物の製造方法」、および「該シリコーンゴムスポンジ形成性組成物を、(C) 成分の熱可塑性樹脂の軟化点以上の温度に加熱して硬化させることを特徴とするシリコーンゴムスポンジの製造方法」に関する。

【0007】

【発明の実施の形態】以下に、本発明のシリコーンゴムスポンジ形成性組成物、該シリコーンゴムスポンジ形成性組成物を加熱硬化してなるシリコーンゴムスポンジ、および、それらの製造方法を詳細に説明する。

(A) ポリオルガノシロキサン生ゴムは、本発明組成物の主成分であり、その分子構造は直鎖状であることが好ましいが、一部分岐を有した直鎖状であってもよい。本成分の重量平均重合度は、通常、1,000~20,000の範囲である。(A)成分中のケイ素原子に結合する基としては、メチル基、エチル基、プロピル基、ブチル基、オクチル基等のアルキル基；フェニル基、トリル基等のアリール基；ビニル基、アリル基、ブテニル基、ヘキセニル基、ヘプテニル基等のアルケニル基；クロロメチル基、3,3,3-トリフルオロプロピル基等のハロ

(特開平4-13738号公報参照)などが提案されている。しかし、この方法で得られたシリコーンゴムスポンジの発泡セルは、均一さや微細さにおいて十分なものではなく、ロール被覆材として要求される性能を満足させることは難しかった。

【0005】

【発明が解決しようとする課題】本発明者らは上記問題を解消すべく鋭意研究した結果、本発明を完成するに至った。即ち、本発明の目的は、均一かつ微細な発泡セルを有するシリコーンゴムスポンジとなり得るシリコーンゴムスポンジ形成性組成物、均一かつ微細な発泡セルを有するシリコーンゴムスポンジ、および、それらの製造方法を提供することにある。

【0006】

【課題の解決手段】本発明は、

- 100重量部、
- 1~500重量部、
- 0.01~10重量部、
- 0.1~10重量部、
- 0.1~10重量部

ゲン化アルキル基等の置換もしくは非置換の一価炭化水素基が例示される。また、分子鎖末端などに水酸基を有してもよい。好ましいアルケニル基はビニル基、次いでヘキセニル基であるが、このアルケニル基の結合位置は限定されず、分子鎖末端、分子鎖側鎖、あるいはその両方であってもよい。後記する(F)成分として白金系触媒と1分子中に少なくとも2個のケイ素原子結合水素原子を有するポリオルガノシロキサンとを併用する場合は、(A)成分は1分子中に少なくとも2個のアルケニル基を持つことが好ましい。また、アルケニル基以外のケイ素原子に結合する基は、メチル基であることが好ましい。

【0008】好ましい(A)成分としては、分子鎖両末端ジメチルビニルシロキシ基封鎖ポリジメチルシロキサン生ゴム、分子鎖両末端トリメチルシロキシ基封鎖ポリジメチルシロキサン生ゴム、分子鎖両末端トリメチルシロキシ基封鎖ジメチルシロキサン・メチルビニルシロキサン共重合体生ゴム、分子鎖両末端ジメチルシロキシ基封鎖ジメチルシロキサン・メチルビニルシロキサン共重合体生ゴム、分子鎖両末端ジメチルヒドロキシシロキシ基封鎖ポリジメチルシロキサン生ゴム、分子鎖両末端ジメチルヒドロキシシロキシ基封鎖ジメチルシロキサン・メチルビニルシロキサン共重合体生ゴム、分子鎖両末端メチルビニルヒドロキシシロキシ基封鎖ジメチルシロキサン・メチルビニルシロキサン共重合体生ゴム、分子鎖両末端ジメチルヘキセニルシロキシ基封鎖ポリジメチルシロキサン生ゴム、分子鎖両末端トリメチルシロキシ基封鎖ジメチルシロキサン・メチルヘキセニルシロ

キサン共重合体生ゴム、分子鎖両末端ジメチルヘキセニルシロキシ基封鎖ジメチルシロキサン・メチルヘキセニルシロキサン共重合体生ゴム、分子鎖両末端ジメチルビニルシロキシ基封鎖ジメチルシロキサン・メチルフェニルシロキサン共重合体生ゴム、分子鎖両末端ジメチルヘキセニルシロキシ基封鎖ジメチルシロキサン・メチルフェニルシロキサン共重合体生ゴム、分子鎖両末端ジメチルビニルシロキシ基封鎖ジメチルシロキサン・メチル(3, 3, 3-トリフルオロプロピル)シロキサン共重合体生ゴム、分子鎖両末端ジメチルヘキセニルシロキシ基封鎖ジメチルシロキサン・メチル(3, 3, 3-トリフルオロプロピル)シロキサン共重合体生ゴム、および、これらのポリオルガノシロキサン生ゴムの2種以上の混合物が例示される。

【0009】(B)無機質充填剤としては、乾式法シリカ、湿式法シリカ等の微粉末状シリカ、それらの表面がオルガノクロシラン、オルガノアルコキシシラン、ヘキサオルガノジシラザン、オルガノシロキサンオリゴマー等で疎水化処理された微粉末状シリカ等で例示される補強性充填剤；石英粉末、けいそう土、重質炭酸カルシウム、軽質炭酸カルシウム、酸化マグネシウム、けい酸カルシウム、マイカ、酸化アルミニウム、水酸化アルミニウム等の準補強性充填剤ないし増量充填剤が例示される。本成分の配合量は多すぎると(A)成分への配合が難しくなるので(A)成分100重量部に対して1~500重量部であり、補強性充填剤は1~100重量部が好ましく、準補強性充填剤ないし増量性充填剤は1~300重量部が好ましい。

【0010】シリコーンゴムスポンジ組成物に導電性を付与するために(B)成分として導電性充填剤を選択しても本発明の目的を損なわない限り差し支えない。かかる導電性充填剤としてカーボンブラック、炭素繊維、グラファイトなどのカーボン系導電剤；金、銀、ニッケルなどの金属粉；導電性酸化亜鉛、導電性酸化チタン、導電性酸化アルミニウム；各種フィラー表面に金属メッキ処理するなどのフィラー表面に導電被覆処理した導電性充填剤が例示される。これら導電性充填剤は、無機充填材と併用しても単独で使用しても差し支えなく、2種類以上の導電性充填材を併用しても本発明の目的を損なわない限り差し支えない。少量の添加で良好な導電性が得られることから、(B)成分は特にカーボンブラックであることが好ましい。好ましいカーボンブラックとしては、通常導電性ゴム組成物に常用されているものを使用し得るが、本発明組成物の硬化阻害を避けるために、低硫黄の原料から製造されたpH6~10の範囲のカーボンブラックであることが好ましい。これらの導電性充填剤の配合量は(A)成分100重量部に対して1~200重量部であり、特に5~100部とすることが好ましい。これは、上記範囲の下限未満であると導電性が得られ無い場合があり、上記範囲の上限をこえるとスポンジ

が得られにくい場合があるからである。

【0011】本発明に使用される(C)熱可塑性樹脂中空粉末は、本発明組成物を加熱硬化させて得られるシリコーンゴムスポンジ中に形成される発泡セルの核になると同時に、その発泡セルの大きさを均一にする働きをする。かかる(C)成分は、熱可塑性樹脂を外殻としてその内部に気体を含有する中空粉末である。ここで、好ましい熱可塑性樹脂としては、シリコーン樹脂、アクリル樹脂、ポリカーボネート樹脂が例示される。この熱可塑性樹脂の軟化点は40~200℃が好ましく、60~180℃がより好ましい。この中空粉末に内包される気体としては、空気または窒素ガスやヘリウムガスなどの不活性ガスが好ましい。(C)成分の大きさは、その平均粒子径が0.1~500μmの範囲が好ましく、1~50μmの範囲がより好ましい。かかる(C)成分は、例えば、溶剤に溶解した熱可塑性樹脂と水との分散液をスプレーノズルから熱気流中に噴霧して、有機溶剤を飛散させるとともに熱可塑性樹脂を粉末化させることにより製造される。本成分の配合量は、(A)成分100重量部に対して0.01~10重量部であり、0.1~5重量部であることが好ましい。

【0012】(D)室温より高い沸点を有する液体は、本発明組成物を加熱硬化させてシリコーンゴムスポンジを形成する際に、揮発して発泡剤としての働きをし、

(C)成分および後述する(E)成分とともに均一かつ微細な発泡セルを形成するために必須とされる成分である。これは、その沸点が室温より低いと本発明組成物を保管中に該液体が揮発してしまい、良好なシリコーンゴムスポンジが得られなくなる場合があるためである。また、(D)成分としては、シリコーンゴムスポンジの形成方法およびその形成条件に応じて、室温より高い適当な沸点を有するものを選定すればよいが、一般に25~200℃の範囲の沸点を有する液体であることが好ましく、50~180℃の範囲の沸点を有する液体であることがより好ましい。

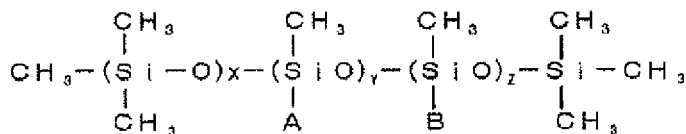
【0013】また、(D)成分は、本発明組成物の保管中に(C)成分の壁材を溶解したり、本発明組成物を加熱硬化させて導電性シリコーンゴムスポンジを形成する際に加熱によって分解したり、他の成分との化学反応を伴ったりしない必要がある。

【0014】かかる(D)成分としては、水；メタノール、エタノール、1-プロパノール、シクロヘキサノール等のアルコール類；エチレングリコールモノエチルエーテル、エチレングリコールモノエチルエーテルアセテート等のエチレングリコール誘導体；ヘキサメチルシクロトリシロキサン、オクタメチルシクロテトラシロキサン等の環状ジメチルシロキサンオリゴマー；分子鎖両末端トリメチルシロキシ基封鎖ジメチルシロキサンオリゴマー；分子鎖両末端ジメチルヒドロキシシロキシ基封鎖ジメチルシロキサンオリゴマーおよびこれらの2種以上

の混合物が例示される。これらの中で水が最も好ましく、次いで環状ジメチルシロキサンオリゴマーが好ましい。水としては、純水、精製水、イオン交換水等と称されている純度の高い水が好ましい。

【0015】(D)成分は、(A)成分と(B)成分とを混合してなるシリコーンゴムベースに直接配合しても良いが、(D)成分の取扱性の向上やシリコーンゴムベースへの分散性の向上を目的として、(D)成分をシリカ粉末などの増粘剤や多孔質粉体等の吸着粉体との混合物の形態でシリコーンゴムベースに配合しても、本発明の目的を損なわない限り差し支えない。また(D)成分が水である場合は、水溶性シリコーンとの混合物やシリコーンオイルを油層とする油中水型のエマルジョンの形で配合することも、本発明の目的を損なわない限り差し支えない。

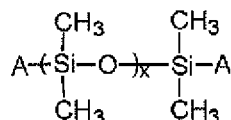
【0016】(D)成分として水を選択し、水溶性シリコーンとの混合物としてシリコーンゴムベースに配合する



{式中、xおよびyは1以上の整数であり、zは0または1以上の整数である。Aは、一般式： $-(\text{CH}_2)_a-\text{O}-(\text{C}_2\text{H}_4\text{O})_p(\text{C}_3\text{H}_5\text{O})_q\text{R}$ (式中、aは1~3の整数、pは1以上の整数、qは0または1以上の整数であり、Rは水素原子またはメチル基、エチル基、プロピル基等の炭素原子数1~4のアルキル基である。) 示される有機基であり、Bは一般式： $-(\text{CH}_2)_n-\text{CH}_3$ (式中、nは7~23の整数である。) で示される有機基である。}

【0018】平均分子式：

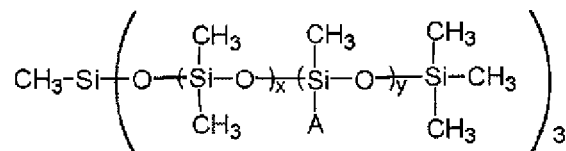
【化2】



(式中、xおよびAは前記と同じである。)

【0019】平均分子式：

【化3】



(式中、x、yおよびAは前記と同じである。)

【0020】かかるポリオキシアルキレン変性シリコーンオイルが良好な水溶性を得るためには、ポリオキシアルキレン部分がポリオキシエチレン、またはオキシエチレンオキシプロピレンコポリマーであり、分子中のその含有量が50重量%以上であるものが好ましい。

場合、その水溶性シリコーンは水に溶解可能なシリコーンであればよく、その種類等は特に限定されない。水溶性シリコーンの水への配合量は特に限定されないが、1~80重量%であることが好ましく、特に5~70重量%であることが好ましい。かかる水に溶解可能なシリコーンとしては、ポリオキシアルキレン変性シリコーンオイル、アミノアルキル基含有シリコーンオイル、アミド基含有シリコーンオイル、カルビノール基含有シロキサンオリゴマー等が挙げられるが、これらの中でもポリオキシアルキレン変性シリコーンオイルが好ましい。かかるポリオキシアルキレン変性シリコーンオイルとしては、下記平均分子式で示されるような側鎖または末端にポリオキシアルキレン基を有するオルガノポリシロキサンが例示される。

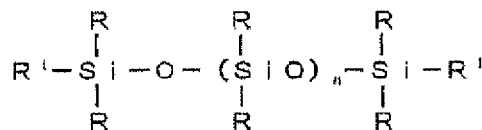
【0017】平均分子式：

【化1】

【0021】また、(D)成分として水を選択し、シリコーンオイルを油層とした油中水型エマルジョンとしてシリコーンゴムベースに配合する場合、かかる油中水型エマルジョンは、水を界面活性剤によりシリコーンオイル中に分散させることにより容易に製造される。この油中水型エマルジョン中の水の含有量は特に限定されないが、1~80重量%であることが好ましく、特に20~70重量%であることが好ましい。

【0022】油層となるシリコーンオイルは、ジオルガノシロキサン単位を主骨格とするオリゴマーないしポリマーであり、液状を呈するものであればよく、その種類は特に限定されない。かかるシリコーンオイルの代表例としては、下記のジオルガノポリシロキサンが例示される。一般式：

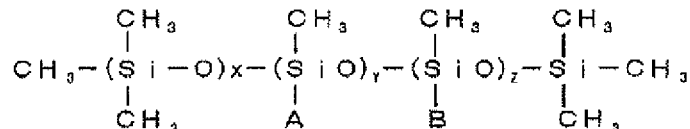
【化4】



(式中、Rは、一価炭化水素基もしくはハロゲン化アルキル基であり、R'はRまたは水酸基である。一価炭化水素基としては、メチル基、エチル基、プロピル基、ブチル基、ペンチル基、ヘキシル基等のアルキル基；ビニル基、アリル基、ヘキセニル基等のアルケニル基；シクロヘキシル基等のシクロアルキル基；β-フェニルエチル基等のアラルキル基；フェニル基等のアリール基等が例示され、ハロゲン化アルキル基としては、3-クロロプロピル基、3,3,3-トリクロロプロピル基が例示される。これらの中でもアルキル基、特にメチル基が好

ましい。nは0以上の整数である。)で表され、25℃における粘度が1~100,000mPa・sの範囲内にあり、好ましくは10~100,000mPa・sの範囲内にある。

【0023】界面活性剤としては、油中水型エマルジョンを形成することのできる界面活性剤であればよく、硬



(式中、x、y、z、AおよびBは前記の通りである。)、上記式Aで示されるポリオキシアルキレン基を分子鎖末端に有するポリジメチルシロキサン、ポリオキシエチレンソルビタン脂肪酸エステル、ポリオキシエチレンソルビット脂肪酸エステル、ポリエチレングリコール脂肪酸エステル、ポリオキシエチレンアルキルエーテル、ポリオキシエチレンアルキルフェニルエーテル等の非イオン系界面活性剤、上記ポリオキシアルキレン基含有オルガノポリシロキサンと上記非イオン系界面活性剤の混合物が例示される。(D)成分の配合量は(A)成分100重量部に対して、0.01~10重量部である。これは上記範囲の上限を超えると、成形されるシリコンスポンジのセルが不均一になりやすく、上記範囲の下限未満となると発泡剤として十分に働かなくなるからである。

【0024】(E)熱分解型発泡剤は、本発明組成物を加熱硬化させてシリコンゴムスポンジを形成する際に、

(D)成分を補助する働きをし、(C)成分および

(D)成分とともに均一かつ微細な発泡セルを形成するために必須とされる成分である。かかる熱分解型発泡剤としては、シリコンゴムスポンジ組成物に使用されている従来公知の無機発泡剤および/または有機発泡剤を使用することができる。

【0025】無機発泡剤としては、炭酸水素ナトリウム、炭酸水素カリウム、水素化ホウ素ナトリウム、カルシウムアジドなどが例示される。中でも炭酸水素ナトリウムが好ましい。

【0026】有機発泡剤としてはアゾビスイソブチロニトリル、2,2'-アゾビス(2,4-ジメチルバレロニトリル)、ジメチル-2,2'-アゾビスイソブチレート、アゾジカルボンアミドなどのアゾ系化合物；N,N'-ジニトロソペンタメチレンテトラミン、N,N'-ジメチル-N,N'-ジニトロソテレフタルアミドなどのニトロソ化合物；p-トルエンスルホンヒドラジド、4,4'-オキシビスベンゼンスルホンヒドラジド、ジフェニルスルホン-3,3'-ジスルホンヒドラジドなどのスルホンヒドラジド化合物；2-プロペン酸ヒドラジド、アセチルヒドラジンなどのカルボニルヒドラジン化合物；4,4'-ジアジドジフェニル、4,4'-ジアジドベンゾフェノン、2,5-ジアジド

化阻害を起こすものでなければその種類は特に限定されない。かかる油中水型エマルジョンを形成するための界面活性剤としては、下記一般式で示されるような側鎖にポリオキシアルキレン基を有するジオルガノポリシロキサン、一般式：

【化5】

トルエンなどのジアジド化合物などが例示される。本成分は1種類のみでも2種類以上の熱分解型発泡剤を併用して使用してもよい。

【0027】(E)成分の配合量は(A)成分100重量部に対して、0.1~10重量部であり、0.1~1.0重量部であることが好ましい。これは上記範囲の下限未満であると十分に発泡したシリコンゴムスポンジが得られず、上記範囲の上限を超えると硬化阻害を起こしたり、得られるシリコンゴムスポンジの耐熱性が悪化することがあるからである。

【0028】(F)硬化剤は本発明組成物を硬化させるための成分であり、その種類等は特に限定されない。代表的な硬化剤としては有機過酸化物が挙げられる。このような有機過酸化物としては、ベンゾイルパーオキサイド、ジ-tert-ブチルパーオキサイド、2,5-ジメチル-2,5-ジ(tert-ブチルパーオキシ)ヘキサン、ビス(オルソメチルベンゾイル)パーオキサイド、ビス(メタメチルベンゾイル)パーオキサイド、ビス(パラメチルベンゾイル)パーオキサイド等のモノメチルベンゾイルパーオキサイド、ビス(2,4-ジメチルベンゾイル)パーオキサイド等のジメチルベンゾイルパーオキサイド、ビス(2,4,6-トリメチルベンゾイル)パーオキサイド等などが例示される。本成分の配合量は、(A)成分~(D)成分の混合物100重量部に対し、0.1~10重量部である。

【0029】また、(A)ポリオルガノシロキサン生ゴムがビニル基で代表されるようなアルケニル基を1分子中に少なくとも2個有するものである場合には、本発明組成物は付加硬化反応による硬化が可能であり、1分子中にケイ素原子結合水素原子を少なくとも2個含有するポリオルガノシロキサンと白金系触媒を併用して硬化剤として使用することができる。該ポリオルガノシロキサンと白金系触媒の併用は、任意に硬化性を変えられることができるので、本発明組成物の硬化剤として好ましい。

【0030】このようなポリオルガノシロキサンとしては、分子鎖両末端トリメチルシロキシ基封鎖ポリメチルハイドロジェンシロキサン、分子鎖両末端トリメチルシロキシ基封鎖ジメチルシロキサン・メチルハイドロジェンシロキサン共重合体、分子鎖両末端ジメチルハイドロジェンシロキシ基封鎖ジメチルシロキサン・メチルハイ

ドロジェンシロキサン共重合体、環状ジメチルシロキサン・メチルヒドロジェンシロキサン共重合体、環状ポリメチルヒドロジェンシロキサン、式： $(\text{CH}_3)_3\text{SiO}_{1/2}$ 単位で表されるシロキサン単位、式： $(\text{CH}_3)_2\text{HSiO}_{1/2}$ 単位で表されるシロキサン単位および式： $\text{SiO}_{4/2}$ で示されるシロキサン単位からなるオルガノポリシロキサン、式： $(\text{CH}_3)_2\text{HSiO}_{1/2}$ 単位で表されるシロキサン単位および式： $\text{CH}_3\text{SiO}_{3/2}$ 単位で示されるシロキサン単位からなるオルガノポリシロキサン、式： $(\text{CH}_3)_2\text{HSiO}_{1/2}$ 単位で表されるシロキサン単位、式： $(\text{CH}_3)_2\text{SiO}_{2/2}$ 単位および式： $\text{CH}_3\text{SiO}_{3/2}$ 単位で示されるシロキサン単位からなるオルガノポリシロキサン、分子鎖両末端ジメチルヒドロジェンシロキシ基封鎖ポリジメチルシロキサン、分子鎖両末端ジメチルヒドロジェンシロキシ基封鎖ジメチルシロキサン・メチルフェニルシロキサン共重合体、分子鎖両末端ジメチルヒドロジェンシロキシ基封鎖ジメチルシロキサン・メチル(3, 3, 3-トリフルオロプロピル)シロキサンおよびこれらのポリオルガノシロキサンの2種以上の混合物が例示される。本ポリオルガノシロキサンの25℃における粘度は特に限定されないが2~100000mPa・sの範囲であることが好ましい。その添加量は本ポリオルガノシロキサン中のケイ素原子結合水素原子の合計モル数と(A)成分中のアルケニル基の合計モル数との比が(0.5:1)~(20:1)となるような量であることが必要である。

【0031】この場合、白金系触媒としては、微粒子白金、塩化白金酸、塩化白金酸のアルコール変性物、白金のキレート化合物、白金とジケトンの錯体、塩化白金酸とオレフィン類の配位化合物、塩化白金酸とアルケニルシロキサンの錯体、およびこれらをアルミナ、シリカ、カーボンブラック等の担体に担持させたものが例示され、これらの中でも塩化白金酸とアルケニルシロキサンの錯体がヒドロシリル化反応用触媒として活性が高いので好ましく、特に特公昭42-22924号公報に開示されているような白金アルケニルシロキサン錯体が好ましい。また、白金系触媒を白金金属原子として0.01重量%以上含有する熱可塑性樹脂から構成される球状微粒子触媒を使用することもできる。白金系触媒中の白金金属の量は、(A)成分100万重量部に対して、0.01~500重量部の範囲内であることが好ましく、特に、これが0.1~100重量部の範囲内であることが好ましい。

【0032】また、(F)成分として白金系触媒と1分子中に少なくとも2個のケイ素原子結合水素原子を有するポリオルガノシロキサンとを併用する場合には、本発明組成物の取扱作業性や貯蔵安定性を向上させるために、2-メチル-3-ブチン-2-オール、2-フェニル-3-ブチン-2-オール、3, 5-ジメチル-1-ヘキシン-3-オール、1-エチニル-1-シクロヘキ

サノール、1, 5-ヘキサジーン、1, 6-ヘプタジーン等のアセチレン系化合物；3, 5-ジメチル-1-ヘキセン-1-イン、3-エチル-3-ブテン-1-イン、3-フェニル-3-ブテン-1-イン等のエン・イン化合物；1, 3-ジビニルテトラメチルジシロキサン、1, 3, 5, 7-テトラビニルテトラメチルシクロテトラシロキサン、1, 3-ジビニル-1, 3-ジフェニルジメチルジシロキサン等のアルケニルシロキサンオリゴマー；メチルトリス(3-メチル-1-ブチン-3-オキシ)シラン等のエチニル基含有ケイ素化合物；トリブチルアミン、テトラメチルエチレンジアミン、ベンゾトリアゾール等の窒素含有化合物；トリフェニルホスフィン等のリン含有化合物；その他、硫黄含有化合物、ヒドロパーオキシ化合物、マレイン酸誘導体、および、これらの2種以上の混合物等の硬化抑制剤を配合することが好ましい。

【0033】これらの硬化抑制剤の配合量は、(A)成分100重量部に対して、3重量部以下でよく、通常0.001~3重量部であり、好ましくは0.01~1重量部である。好ましい硬化抑制剤は上記で例示したようなアセチレン系化合物であり、これらは組成物の十分な保存安定性と迅速な硬化性とをバランスよく発揮させる。

【0034】その他任意の成分として、焼成シリカ、水酸化アルミニウム、酸化アルミニウム、石英粉末、けいそう土、アルミノケイ酸塩、重質炭酸カルシウム、軽質炭酸カルシウム、酸化マグネシウム、けい酸カルシウム、マイカ等の無機質充填剤；酸化鉄、二酸化チタンなどの顔料；酸化セリウム、水酸化セリウム、等の耐熱剤；炭酸マンガ、炭酸亜鉛、ヒュームド二酸化チタン等の難燃剤を含有してもよい。これらの無機質充填剤は未処理のものを使用してもよく、また予め、表面処理剤により処理したものをを用いてもよい。

【0035】さらに本発明組成物には、分子鎖両末端トリメチルシロキシ基封鎖ポリジメチルシロキサン、分子鎖両末端ジメチルヒドロキシシロキシ基封鎖ポリジメチルシロキサン、分子鎖両末端トリメチルシロキシ基封鎖ジメチルシロキサン・メチルフェニルシロキサン共重合体、分子鎖両末端トリメチルシロキシ基封鎖ジメチルシロキサン・ジフェニルシロキサン共重合体、分子鎖両末端ジメチルヒドロキシシロキシ基封鎖ジメチルシロキサン・メチルフェニルシロキサン共重合体、分子鎖両末端トリメチルシロキシ基封鎖ジメチルシロキサン・メチル(3, 3, 3-トリフルオロプロピル)シロキサン共重合体などの、ケイ素原子結合アルケニル基およびケイ素原子結合水素原子を有しない液状ポリオルガノシロキサン；シリコーンゴム粉、シリコーン樹脂粉などのシリコーン粉状添加剤；ステアリン酸、ステアリン酸カルシウム、ステアリン酸亜鉛、ステアリン酸セリウムなどの離型剤；接着促進剤などを含有してもよい。

【0036】本発明組成物は、上記のような(A)成分～(F)成分、あるいは、さらに必要に応じてその他の成分を加えて均一に混合することにより容易に製造できるが、(B)成分として補強性充填剤を含有する場合は、(A)成分と該補強性充填剤と必要に応じて補強性充填剤の表面処理剤とを加熱下混練してシリコンゴムベースを製造した後、他成分と混合することが好ましい。製造装置としては、ニーダーミキサー、連続混練押出機等の混合装置あるいは混練装置が例示される。

【0037】本発明組成物からシリコンゴムスポンジを製造するには、本発明組成物を、(C)成分を構成する熱可塑性樹脂の軟化点以上の温度に加熱して硬化させればよい。その際、本発明組成物は発泡しつつ硬化して、シリコンゴムスポンジを形成する。本発明組成物は押出成形、金型を用いた加圧成形においても良好なシリコンゴムスポンジを形成できるので、シート状、リング状、ヒモ状、チューブ状など種々の形状のシリコンゴムスポンジを成形することができ、また、金属や他の有機樹脂との複合成形物の生産にも好適であるという特徴がある。かくして得られたシリコンゴムスポンジは、均一かつ微細な発泡セルを有し、例えば、建築用部材の気密保持用ガスケット、耐火ガスケット、シール材、Oリング、クッション材、さらには複写機ロールの表面被覆材等として有用である。

【0038】

【実施例】次に、本発明を実施例および参考例により説明する。実施例中、部とあるのは重量部のことであり、粘度は25℃における値である。

【0039】

【参考例1】メチルシロキサン単位とメチルフェニルシロキサン単位とから構成され、そのモル比が22:78であるシリコン樹脂(軟化点80℃、比重1.20)をジクロロメタンに溶解した溶液(固形分量30重量%)を100cc/分の供給量、純水を25cc/分の供給量でダイナミックミキサー内に液送し混合して水分散液とした。次いで、この水分散液を2流体ノズルを使って、窒素ガス気流としたスプレードライヤー内に連続的に噴霧した。この時の窒素ガスの熱気流温度は70℃であり、圧力は0.05MPaであった。得られたシリコン樹脂中空粉体を純水100部と非イオン界面活性剤(トリメチルノナノールのエチレンオキサイド付加物)1部からなる水溶液に24時間浸漬し、浮遊したシリコン樹脂中空粉体を分別し捕集した。得られたシリコン樹脂中空粉体は平均粒子径が40μmであり、その外殻の平均厚さが4μmであり、その内部に窒素ガスを内包していた。

【0040】

【参考例2】平均分子式が、 $\text{Me}_3\text{SiO}-(\text{Me}_2\text{SiO})_7-(\text{MeR}^2\text{SiO})_3-\text{SiMe}_3$ [式中、Meはメチル基であり、 R^2 は式: $-(\text{CH}_2)_2-\text{O}-(\text{C}_2\text{H}$

$_4\text{O})_{12}-\text{H}$ で表される基を示す。]で示される粘度400mPa・sの水溶性のポリオキシアルキレン変性シリコンオイル40部とイオン交換水60部をフラスコ中で均一に混合して水溶液(以下、水溶液A)を調製した。

【0041】

【参考例3】平均分子式が、 $\text{Me}_3\text{SiO}-(\text{Me}_2\text{SiO})_{70}-(\text{MeR}^2\text{SiO})_3-\text{SiMe}_3$ [式中、Me、 R^2 は上記と同様である。]で示される粘度1600mPa・sのポリオキシアルキレン変性シリコンオイル10部と粘度100mPa・sの分子鎖両末端トリメチルシロキシ基封鎖ポリジメチルシロキサン50部とをフラスコに入れ強く攪拌した。次いで、これに、イオン交換水40部を徐々に添加して混合することにより、粘度100mPa・sの分子鎖両末端トリメチルシロキシ基封鎖ポリジメチルシロキサンを油層とした油中水型エマルジョンを調製した。

【0042】

【実施例1】ジメチルシロキサン単位99.85モル%とメチルビニルシロキサン単位0.15モル%とからなる分子鎖両末端ジメチルビニルシロキシ基封鎖ジメチルシロキサン・メチルビニルシロキサン共重合体生ゴム(重合度3000)100部、粘度60mPa・sの分子鎖両末端ジメチルヒドロキシシロキシ基封鎖ジメチルシロキサンオリゴマー10部、BET法による比表面積200m²/gの乾式法シリカ40部をニーダーミキサーに入れ加熱下均一になるまで混練してシリコンゴムベースを作製した。次いで、このシリコンゴムベース100部に対して、25mPa・sの分子鎖両末端トリメチルシロキシ基封鎖ジメチルシロキサン・メチルヒドロジェンシロキサン共重合体(ケイ素原子結合水素原子含有量0.8重量%)1.0部(本分子鎖両末端トリメチルシロキシ基封鎖ジメチルシロキサン・メチルヒドロジェンシロキサン共重合体中のケイ素原子結合水素原子のモル数と上記ビニル基含有ポリジオルガノシロキサン生ゴム中のケイ素原子結合ビニル基のモル数との比が4.9となる量)、ヒドロシリル化反応抑制剤として1-エチニル-1-シクロヘキサノール0.015部、塩化白金酸とテトラメチルジビニルジシロキサンとの錯体(白金含有量0.6重量%)を0.06部、参考例1で得られたシリコン樹脂中空粉体1.0部、蒸留水0.5部、炭酸水素ナトリウム0.5部を添加し、2本ロール上で均一に混練してシリコンゴムスポンジ形成性組成物を得た。この組成物を厚さ5mmのシート状とした後、250℃の加熱炉中に入れ10分間加熱し硬化させてシリコンゴムスポンジシートを得た。このシリコンゴムスポンジシートの発泡セルを観察したところ、発泡セルはほぼ均一であり、そのセルの大きさは直径0.1~0.4mmであった。

【0043】

【実施例2】65mmφの1軸押出機に、実施例1で得られたシリコンゴムスポンジ形成性組成物を投入してチューブ状成形品として押出した後、250℃の加熱炉中で4分間加熱してシリコンゴムスポンジチューブを得た。このシリコンゴムスポンジチューブの発泡セルはほぼ均一であり、その発泡セルの大きさは直径0.1~0.5mmであった。

【0044】

【実施例3】キャビティの形状が10mm×40mm×80mmの直方体であり、その容積が32cm³である圧縮成形用金型に、実施例1で得られたシリコンゴムスポンジ形成性組成物16cm³を仕込み、170℃で15分間加熱してシリコンゴムスポンジ成形物を得た。このシリコンゴムスポンジ成形物の外形は金型のキャビティ形状に忠実であり、その発泡セルの大きさは直径0.1~0.4mmであり、ほぼ均一であった。

【0045】

【実施例4】ジメチルシロキサン単位99.85モル%とメチルビニルシロキサン単位0.15モル%とからなる分子鎖両末端ジメチルビニルシロキシ基封鎖ジメチルシロキサン・メチルビニルシロキサン共重合体生ゴム（重合度3000）100部、粘度60mPa・sの分子鎖両末端ジメチルヒドロキシシロキシ基封鎖ジメチルシロキサンオリゴマー10部、比表面積200m²/gの乾式法シリカ40部をニーダーミキサーに入れ加熱下均一になるまで混練してシリコンゴムベースを作製した。次いで、このシリコンゴムベース100部に対して、25mPa・sのトリメチルシロキシ基封鎖ジメチルシロキサン・メチルハイドロジェンシロキサン共重合体（ケイ素原子結合水素原子含有量0.8重量%）1.0部（本分子鎖両末端トリメチルシロキシ基封鎖ジメチルシロキサン・メチルハイドロジェンシロキサン共重合体中のケイ素原子結合水素原子のモル数と上記ビニル基含有ポリジオルガノシロキサン生ゴム中のケイ素原子結合ビニル基のモル数との比が4.9となる量）、ヒドロシリル化反応抑制剤として1-エチニル-1-シクロヘキサノール0.015部、塩化白金酸とテトラメチルジビニルジシロキサンとの錯体（白金含有量0.6重量%）を0.06部、参考例1で得られたシリコン樹脂中空粉体1.0部、蒸留水0.5部、分解温度122℃のアゾジカルボンアミド系有機発泡剤（商品名ビニホルAK#2）0.5部、硬化助剤として2-5-ジメチル-2-5-ジ（ターシャリーブチルパーオキシ）ヘキサノール0.5部を添加し、2本ロール上で均一に混練してシリコンゴムスポンジ形成性組成物を得た。この組成物を厚さ5mmのシート状とした後、250℃の加熱炉中に入れ10分間加熱し硬化させてシリコンゴムスポンジシートを得た。このシリコンゴムスポンジシートの発泡セルを観察したところ、発泡セルはほぼ均一であり、そのセルの大きさは直径0.1~0.4mmであった。

【0046】

【実施例5】キャビティの形状が10mm×40mm×80mmの直方体であり、その容積が32cm³である圧縮成形用金型に、実施例4で得られたシリコンゴムスポンジ形成性組成物10cm³を仕込み、170℃で15分間加熱してシリコンゴムスポンジ成形物を得た。このシリコンゴムスポンジ成形物の外形は金型のキャビティ形状に忠実であり、その発泡セルの大きさは直径0.1~0.5mmであり、ほぼ均一であった。

【0047】

【実施例6】ジメチルシロキサン単位99.85モル%とメチルビニルシロキサン単位0.15モル%とからなる分子鎖両末端ジメチルビニルシロキシ基封鎖ジメチルシロキサン・メチルビニルシロキサン共重合体生ゴム（重合度3000）100部、粘度60mPa・sの分子鎖両末端ジメチルヒドロキシシロキシ基封鎖ジメチルシロキサンオリゴマー5部、比表面積200m²/gの乾式法シリカ20部をニーダーミキサーに入れ加熱下均一になるまで混練してシリコンゴムベースを得た。このシリコンゴムベース125部にアセチレンブラック（デンカブラック；電気化学工業株式会社製）15部を添加し室温にて均一になるまで混練し導電性シリコンゴムベースを作製した。次いで、この導電性シリコンゴムベース100部に対して、25mPa・sのトリメチルシロキシ基封鎖ジメチルシロキサン・メチルハイドロジェンシロキサン共重合体（ケイ素原子結合水素原子含有量0.8重量%）1.0部（本分子鎖両末端トリメチルシロキシ基封鎖ジメチルシロキサン・メチルハイドロジェンシロキサン共重合体中のケイ素原子結合水素原子のモル数と上記ビニル基含有ポリジオルガノシロキサン生ゴム中のケイ素原子結合ビニル基のモル数との比が4.5となる量）、ヒドロシリル化反応抑制剤として1-エチニル-1-シクロヘキサノール0.015部、塩化白金酸とテトラメチルジビニルジシロキサンとの錯体（白金含有量0.6重量%）を0.06部、参考例1で得られたシリコン樹脂中空粉体1.0部、蒸留水0.5部、炭酸水素ナトリウム0.5部を添加し、2本ロール上で均一に混練して導電性シリコンゴムスポンジ形成性組成物を得た。この組成物を厚さ5mmのシート状とした後、250℃の加熱炉中に入れ10分間加熱し硬化させて導電性シリコンゴムスポンジシートを得た。この導電性シリコンゴムスポンジシートの発泡セルを観察したところ、発泡セルはほぼ均一であり、そのセルの大きさは直径0.1~0.4mmであった。

【0048】

【実施例7】65mmφの1軸押出機に、実施例6で得られた導電性シリコンゴムスポンジ形成性組成物を投入してチューブ状成形品として押出した後、250℃の加熱炉中で4分間加熱して導電性シリコンゴムスポンジチューブを得た。この導電性シリコンゴムスポンジ

チューブの発泡セルはほぼ均一であり、その発泡セルの大きさは直径0.1~0.5mmであった。

【0049】

【実施例8】キャビティの形状が10mm×40mm×80mmの直方体であり、その容積が32cm³である圧縮成形用金型に、実施例6で得られた導電性シリコーンゴムスポンジ形成性組成物16cm³を仕込み、170℃で15分間加熱して導電性シリコーンゴムスポンジ成形物を得た。この導電性シリコーンゴムスポンジ成形物の外形は金型のキャビティ形状に忠実であり、その発泡セルの大きさは直径0.1~0.4mmであり、ほぼ均一であった。

【0050】

【実施例9】実施例6において、蒸留水に変えて参考例2で作製した水溶液Aを導電性シリコーンゴムベース100部に対して1.0部添加した以外は実施例6と同様にして導電性シリコーンゴムスポンジ形成性組成物を得た。この組成物を厚さ5mmのシート状とした後、250℃のオーブンに投入し、10分間加熱硬化させて導電性シリコーンゴムスポンジシートを得た。この導電性シリコーンゴムスポンジシートの発泡セルは均一であり、その発泡セルの大きさは直径0.1~0.5mmであった。

【0051】

【実施例10】実施例6において、蒸留水に変えて参考例3で作製した油中水型エマルジョンを導電性シリコーンゴムベースコンパウンド100部に対して1.2部添加した以外は実施例6と同様にして導電性シリコーンゴムスポンジ形成性組成物を得た。この組成物を厚さ5mmのシート状とした後、250℃のオーブンに投入し、10分間加熱硬化させて導電性シリコーンゴムスポンジシートを得た。この導電性シリコーンゴムスポンジシートの発泡セルは均一であり、その発泡セルの大きさは直径0.1~0.5mmであった。

【0052】

【実施例11】ジメチルシロキサン単位99.85モル%とメチルビニルシロキサン単位0.15モル%とからなる分子鎖両末端ジメチルビニルシロキシ基封鎖オルガノポリシロキサン生ゴム（重合度3000）100部、粘度60mPa・sの分子鎖両末端ジメチルヒドロキシシロキシ基封鎖ジメチルシロキサンオリゴマー5部、比表面積200m²/gの湿式法シリカ40部をニーダーミキサーに入れ加熱下均一になるまで混練してシリコーンゴムベースを作製した。次いで、このシリコーンゴムベース100部に対して、25mPa・sのトリメチルシロキシ基封鎖ジメチルシロキサン・メチルヒドロジェンシロキサン共重合体（ケイ素原子結合水素原子含有量0.8重量%）1.0部（本分子鎖両末端トリメチルシロキシ基封鎖ジメチルシロキサン・メチルヒドロジェンシロキサン共重合体中のケイ素原子結合水素原子の

モル数と上記ビニル基含有ポリジオルガノシロキサン生ゴム中のケイ素原子結合ビニル基のモル数との比が4.6となる量）、ヒドロシリル化反応抑制剤として1-エチニル-1-シクロヘキサノール0.015部、塩化白金酸とテトラメチルジビニルジシロキサンとの錯体（白金含有量0.6重量%）を0.06部、参考例1で得られたシリコーン樹脂中空粉体1.0部、蒸留水0.5部、炭酸水素ナトリウム0.5部を添加し、2本ロール上で均一に混練してシリコーンゴムスポンジ形成性組成物を得た。この組成物を厚さ5mmのシート状とした後、250℃の加熱炉中に入れ10分間加熱し硬化させてシリコーンゴムスポンジシートを得た。このシリコーンゴムスポンジシートの発泡セルを観察したところ、発泡セルはほぼ均一であり、そのセルの大きさは平均直径0.1~0.4mmであった。

【0053】

【実施例12】ジメチルシロキサン単位99.85モル%とメチルビニルシロキサン単位0.15モル%とからなる分子鎖両末端ジメチルビニルシロキシ基封鎖ジメチルシロキサン・メチルビニルシロキサン共重合体生ゴム（重合度3000）100部、粘度60mPa・sの分子鎖両末端ジメチルヒドロキシ基封鎖ジメチルシロキサンオリゴマー10部、比表面積200m²/gの乾式法シリカ40部をニーダーミキサーに入れ加熱下均一になるまで混練してシリコーンゴムベースを作製した。次いで、このシリコーンゴムベース100部に対して、P-メチルベンゾイルパーオキシド0.5部、ジクミルパーオキシド1.0部、参考例1で得られたシリコーン樹脂中空粉体1.0部、蒸留水0.5部、分解温度122℃のアゾジカルボンアミド系有機発泡剤（商品名ビニホールAK#2）0.5部、を添加し、2本ロール上で均一に混練してシリコーンゴムスポンジ形成性組成物を得た。この組成物を厚さ5mmのシート状とした後、250℃の加熱炉中に入れ10分間加熱し硬化させてシリコーンゴムスポンジシートを得た。このシリコーンゴムスポンジシートの発泡セルを観察したところ、発泡セルはほぼ均一であり、そのセルの大きさは直径0.1~0.4mmであった。

【0054】

【比較例1】実施例1において、シリコーン樹脂中空粉体を添加しなかった以外は実施例1と同様にしてシリコーンゴムスポンジ形成性組成物を得た。この組成物を厚さ5mmのシート状成形品とした後、250℃の加熱炉に入れ10分間加熱し硬化させてシリコーンゴムスポンジシートを得た。このシリコーンゴムスポンジシートの発泡セルは不均一であり、直径3mm以上の発泡セルも多数認められた。

【0055】

【比較例2】65mmφの1軸押出機に、比較例1で得られたシリコーンゴムスポンジ形成性組成物を投入して

チューブ状に押出した後、250℃の加熱炉中で5分間加熱し硬化させてシリコーンゴムスポンジチューブを得た。その発泡セルは不均一であり、直径3mm以上の発泡セルも多数認められた。

【0056】

【比較例3】キャビティの形状が10mm×40mm×80mmの直方体であり、その容積が32cm³である圧縮成形用金型に、比較例1で得られたシリコーンゴムスポンジ形成性組成物16cm³を仕込み、170℃で15分間加熱して導電性シリコーンゴムスポンジ成形物を得た。このシリコーンゴムスポンジ成形物の外形は金型のキャビティ形状に忠実であったが、その発泡セルは不均一であり、直径3mm以上の発泡セルも多数認められた。

【0057】

【比較例4】実施例1において、蒸留水を添加しなかった以外は実施例1と同様にしてシリコーンゴムスポンジ形成性組成物を得た。この組成物を厚さ5mmのシート状成形品とした後、250℃の加熱炉に入れ10分間加熱し硬化させてシリコーンゴムスポンジシートを得た。このシリコーンゴムスポンジシートの発泡は十分ではなかった。

【0058】

【比較例5】実施例4において、シリコーン樹脂中空粉体を添加しなかった以外は実施例4と同様にしてシリコーンゴムスポンジ形成性組成物を得た。この組成物を厚さ5mmのシート状とした後、250℃のオーブンに投入し、10分間加熱硬化させてシリコーンゴムスポンジシートを得た。このシリコーンゴムスポンジシートの発泡セルは不均一であり、直径3mm以上の発泡セルも多数認められた。

【0059】

【比較例6】実施例4において、蒸留水を添加しなかった以外は実施例4と同様にしてシリコーンゴムスポンジ形成性組成物を得た。この組成物を厚さ5mmのシート状成形品とした後、250℃の加熱炉に入れ10分間加

熱し硬化させてシリコーンゴムスポンジシートを得た。このシリコーンゴムスポンジシートの発泡は十分ではなかった。

【0060】

【比較例7】実施例6において、シリコーン樹脂中空粉体を添加しなかった以外は実施例6と同様にして導電性シリコーンゴムスポンジ形成性組成物を得た。この組成物を厚さ5mmのシート状とした後、250℃のオーブンに投入し、10分間加熱硬化させて導電性シリコーンゴムスポンジシートを得た。この導電性シリコーンゴムスポンジシートの発泡セルは不均一であり、直径3mm以上の発泡セルも多数認められた。

【0061】

【比較例8】実施例12において、シリコーン樹脂中空粉体を添加しなかった以外は実施例12と同様にしてシリコーンゴムスポンジ形成性組成物を得た。この組成物を厚さ5mmのシート状とした後、250℃のオーブンに投入し、10分間加熱硬化させてシリコーンゴムスポンジシートを得た。このシリコーンゴムスポンジシートの発泡セルは不均一であり、直径3mm以上の発泡セルも多数認められた。

【0062】

【発明の効果】本発明のシリコーンゴムスポンジ形成性組成物は、(A)成分～(F)成分からなり、特に、(C)熱可塑性樹脂中空粉体、(D)沸点が室温より高い液状化合物および(E)熱分解型発泡剤を含有しているので、硬化後、均一かつ微細な発泡セルを有するシリコーンゴムスポンジになり得るという特徴を有し、また本発明のシリコーンゴムスポンジ形成性組成物の製造方法はかかるシリコーンゴムスポンジ形成性組成物を効率よく製造できるという特徴を有する。本発明のシリコーンゴムスポンジは前記シリコーンゴムスポンジ形成性組成物を加熱し硬化してなるので均一かつ微細な発泡セルを有するという特徴を有し、本発明のシリコーンゴムスポンジの製造方法はかかるシリコーンゴムスポンジを効率よく製造できるという特徴を有する

フロントページの続き

(51)Int. Cl.⁷

識別記号

F I

テ-マ-ト' (参考)

C 08 K 5/14

C 08 K 5/14

5/5415

5/5415

C 08 L 83/04

C 08 L 83/04

/(C 08 L 83/04

101:00

101:00)

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Fターム(参考) 4F074 AA90 AA92 AA95 AA97 AC32
 AE07 AG01 BA03 BA13 BA34
 BA84 BB21 BB22 BB23 CA22
 CA23 CA24 CB62 CB84 CC04Y
 CC06Y DA33 DA39

4J002 BG003 CG003 CP033 CP042
 CP121 DA036 DE027 DE076
 DE146 DE179 DE218 DE236
 DF008 DJ006 DJ016 DJ056
 DK008 EC037 ED007 EH157
 EK009 EQ018 EQ028 ES008
 ET008 EV268 EX037 EZ009
 FA103 FB096 FD016 FD116
 FD149 FD203 FD327 FD328
 GJ02 GN00 GQ00 GT00